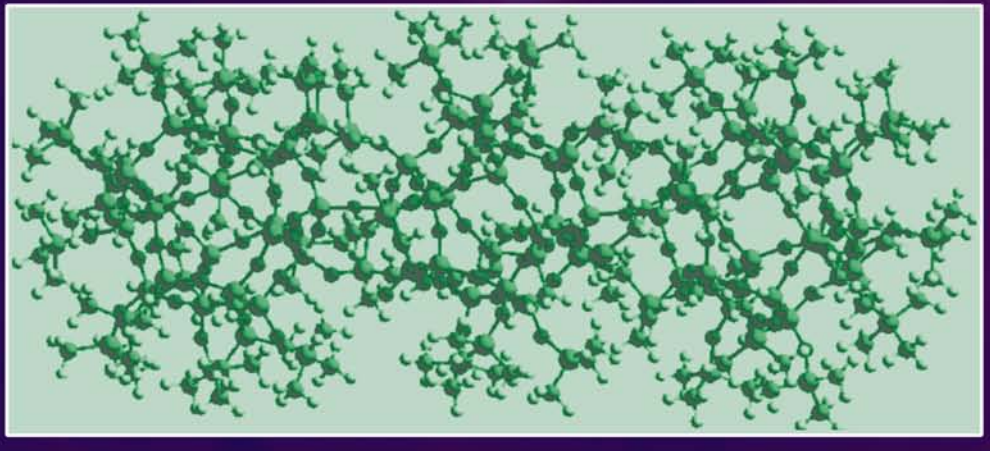
HANDBOOK OF
PRESSURE-SENSITIVE ADHESIVES AND PRODUCTS

TECHNOLGY OF PRESSURE-SENSITIVE ADHESIVES AND PRODUCTS



EDITED BY

ISTVÁN BENEDEK

MIKHAIL M. FELDSTEIN

CRC Press
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TECHNOLOGY OF PRESSURE-SENSITIVE ADHESIVES AND PRODUCTS

Handbook of Pressure-Sensitive Adhesives and Products

Fundamentals of Pressure Sensitivity

Technology of Pressure-Sensitive Adhesives and Products

Applications of Pressure-Sensitive Products

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Preface

Since their introduction almost a century ago, pressure-sensitive adhesives (PSAs) have been successfully applied in many fields. They have experienced an astonishing growth rate, and their installed manufacturing and converting capacity has also sharply increased. However, a specific engineering technology for PSAs, surprisingly a special science, appears to be lacking. The application of PSAs requires a thorough knowledge of basic rheological and viscoelastic phenomena. Therefore, there is a need to investigate and summarize the most important features of PSA technology and explain the phenomena scientifically.

Based on our experience in both scientific activity and industrial areas, as well as on the special knowledge of outstanding scientists and technologists as contributors, we have addressed all aspects of PSAs in the form of a handbook. The huge volume of data accumulated in this field over the past decade presents a delicate problem due to the gap between the fundamentals of pressure-sensitive materials and their practice. The volume and diversification of the data as well as the boundary between theory and application imposed the need to impart our treatise in three books. *Fundamentals of Pressure Sensitivity* discusses the fundamentals of pressure sensitivity, whereas *Technology of Pressure-Sensitive Adhesives and Products* and *Applications of Pressure-Sensitive Products* focus on its practice.

The destination of this handbook is twofold. On one hand, it is addressed to scientists focusing on the fundamental processes underlying the complex phenomenon of pressure-sensitive adhesion; on the other hand, it is intended for industrial researchers who are involved in the practical application of these fundamentals for the development of various products and specialists working in various end-use domains of PSPs. *Fundamentals of Pressure Sensitivity* contains a detailed characterization of the processes occurring in pressure-sensitive materials at all stages of the life of an adhesive joint: during its formation under compressive force, under service as the bonding force is removed, and under adhesive bond fracture, when the major type of deformation is extension.

Based on various aspects of macromolecular science and physics described in *Fundamentals of Pressure Sensitivity*, in *Technology of Pressure-Sensitive Adhesives and Products* the main aspects of pressure-sensitive technology are described, including the raw materials, equipment, and technology required to formulate and manufacture PSAs and to construct and manufacture PSPs.

Applications of Pressure-Sensitive Products describes the main classes and representatives of PSPs, their competitors, end-uses, application domains, and application technologies, and their tests.

Chapter 1 of this book "Pressure-Sensitive Raw Materials," is a short presentation of the chemical basis of PSAs, allowing further discussion regarding the details of each class of raw materials or PSA formulation. Although the main synthesis of the pressure-sensitive raw materials (elastomers and viscous additives) is the subject of exhaustive works specializing in macromolecular chemistry and technology, advances in the in-line manufacture technology of PSAs demand discussion of the synthesis and technology of pressure-sensitive raw materials. The monomers used, the polymerization technology, polymer analogous reaction-based technology, and the formulation of off-line manufactured PSA raw materials are described in comparison to in-line synthesis. The major basic products of pressure-sensitive formulation, that is, the elastomers (random, alternative, and block copolymers), the viscoelastic materals (e.g., acrylics and other vinyl polymers, silicones, etc.), and additives, are briefly presented, allowing their detailed discussion in Chapters 2 through 9 of this book. As suggested many years ago by Benedek in *Pressure-Sensitive Adhesives Technology* (Dekker, 1996), and as discussed in Section 1.3, the science and practice of PSPs reveal that they are composite materials. This means that their construction plays an equivalent role with their constituting materials.

The specific features of rubber-based PSAs are examined in Chapter 2 of this book, "Rubber-Based Pressure-Sensitive Adhesives." Natural rubber-based PSAs were the first self-adhesive products used for the manufacture of PSPs. Although natural rubber is self-adhesive, most elastomers must be mixed with plasticizers and tackifiers (i.e., formulated) to display usable pressure sensitivity. The special structure of common elastomers, their high, so-called rubberlike elasticity, related to their partially cross-linked structure allowing strain hardening, offers a large range of modalities (tackification, plasticization, cross-linking, filling, etc.) for their formulation. This chapter deals with the specific features of rubber-based adhesives, allowing their comparative examination.

The description of block copolymer-based hot-melt pressure-sensitive adhesives is the subject of Chapter 3 of this book. As discussed in Chapter 1, developments in macromolecular chemistry allowed the synthesis of rubber- and plasticlike polymers. Such so-called thermoplastic elastomers (TPEs) have a partially cross-linked structure like common elastomers, which imparts elasticity. In this case, the partially cross-linked structure (segregation) is based on physical, thermally instable bonding, which makes the thermal, plasticlike processing of such elastomers feasible. Advances in macromolecular chemistry and technology allowed the synthesis of a broad range of TPEs based on various monomers and with different build-ups. In Chapter 3 the distinctive features of the mechanical and adhesive properties of styrene–diene-based block copolymers are considered and compared with the properties of PSAs of others classes. The synthesis methods of styrene–diene block copolymers with different structures (e.g., linear, radial, tapered, etc.) are described. Star- and oligomer-modified star polymers and multiblock polymers are examined in comparison with olefin- and acrylate-based block copolymers. Tackification, based on selective compatibility, is investigated (see also Chapter 8). The features of block copolymers, that is, their mechanical properties (tensile strength, creep, etc.) and adhesive properties (tack, peel resistance, and shear resistance) are investigated. Processing and limitations in use are also discussed.

Polyisobutene-based pressure-sensitive adhesives are evaluated in Chapter 4 of this book. In the range of elastomer-based PSPs, polyisobutene (PIB)-based PSAs constitute a special class, with an old and large application field. Owing to their classic synthesis, which allowed the manufacture of various, well-characterized products, PIBs were used for pressure-sensitive tapes in different end-use domains (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Owing to their systematic investigation (including macromolecular chemistry and physics and contact mechanics), their application performance characteristics can be easily related to their fundamental aspects; that is, they serve as model compounds. The role of high- and low-molecular-weight PIB fractions in adhesive performance is described, along with the impact of molecular weight distribution, chain entanglements, M_e (cross-linking), etc. The advantages and drawbacks of PIB adhesives, compared with other PSAs, are also discussed.

Chapter 5 of this book, "Acrylic Adhesives," describes the most important viscoelastic polymers used for PSAs. Acrylic copolymers were the first class of synthetic polymers used for PSAs. Acrylics are also available as solvent-based, water-based, and 100% solids. Acrylics are also supplied as acrylic rubbers and thermoplastic elastomers. Owing to their very large monomer basis, their copolymerizability by various procedures (which include in-line technology-required radiation-induced polymerization), their built-in pressure sensitivity (which can be easily regulated by tackification, cross-linking, etc.), and their excellent aging and physiological properties, acrylics remain the main class of pressure-sensitive raw materials. In this chapter the relationship between the monomer composition of acrylic polymers and their adhesive behavior is discussed. Synthesis and the tools to control performance, that is, macromerization, radiation-induced and chemical curing, and tackification, are also described. Water- and solvent-based adhesives are examined in comparison.

Chapter 6 of this book is focused on silicone pressure-sensitive adhesives. Silicones are a class of heteropolymers that (due to the special nature of the silicone–carbon bond) display valuable application properties; they provide increased thermal resistance coupled with favorable physiological characteristics (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Owing to various chemical possibilities, various synthesis methods can be used to incorporate different monomers in polysiloxane, and due to the regulation of the organic–inorganic ratio in the polymer and other macromolecular characteristics, fine-tuning of the adhesive properties is possible, which leads, *ad absurdum,* to nonadhesive and adhesive products (see also Chapter 9 of this book).

Hydrophilic adhesives are the subject of Chapter 7 of this book. In the first part of this chapter, the major types of hydrophilic adhesives and bioadhesives are described. As demonstrated in Chapter 10 of *Fundamentals of Pressure Sensitivity*, at a molecular level, pressure-sensitive adhesion of polymer materials requires a balance between a high value of cohesion energy and a large free volume. This fundamental factor underlies the Corplex™ technology for development of new adhesive materials through the blending of nonadhesive polymer components. In such adhesives the high cohesion energy results from the formation of either hydrogen or electrostatic bonds between functional groups of two complementary polymer chains (noncovalent cross-linking of the polymers in the blend). The large free volume results from either the location of the reacting functional groups at the ends of the oligomer chains or the plasticization of the interpolymer complex. Such hydrogels (their construction and performances) are

examined in comparison with other hydrogels. The practical aspects of the use of such hydrophilic PSAs are also discussed in *Applications of Pressure-Sensitive Products*.

In Chapter 8 of this book, the role and methods of formulation of various raw material classes (presented in previous chapters) are discussed. Pressure-sensitive adhesives are based on elastomers mixed with viscous components (e.g., tackifiers and plasticizers), which impart them with pressure sensitivity, or allows regulation based on control of glass transition temperature and elasticity modulus. Other physical or chemical procedures (e.g., filling and cross-linking) affect pressure sensitivity as well. Such design modalities are the subject of formulation. This chapter describes the role of formulation and the methods of formulation to introduce the reader to the detailed discussion of tackification and cohesion control. As described in Chapter 1, after their synthesis, the main part of adhesive raw materials must be mixed with various other components to achieve the manufacture and application properties of the PSA. The role of formulation is to ensure the adhesion-related characteristics (e.g., tack, peel resistance, and shear resistance), end-use-related characteristics (e.g., water, temperature, and environmental resistance), and the technology-related performances, including coatibility of the PSA and convertability of the PSP. Such requirements are fulfilled using various formulation methods (e.g., tackification, cross-linking, filling, and special chemical or technological additives).

Silicone release coating technology, discussed in Chapter 9 of this book, constitutes a principal component of PSPs. Generally, PSPs are temporarily laminated, whereas delamination is allowed by using a dehesive, release-coated carrier material (liner) to protect the adhesive-coated carrier material and to allow its processing as a continuous web. Although various release coatings were developed on very different chemical bases, silicone-based release coatings are the sole materials with an almost general usability. In this chapter the functioning, grades, build-up, manufacture, and coating technology of silicone-based release coatings are discussed.

Chapter 10 of this book describes the manufacture of pressure-sensitive products. Using the raw materials presented in Chapters 1 through 9 and the principles of formulation discussed in Chapter 8, PSAs are manufactured and processed in PSPs. Such technology comprises the manufacture of web-components (e.g., adhesive, release, and carrier), the manufacture of the web, that is, the coating of the carrier with the PSA (using various methods), and conversion of the pressure-sensitive web (laminate) into a finished web-like or discrete PSP (e.g., label, tape and protective film) by means of various overcoating (e.g., lamination, printing and lacquering) and confectioning procedures (e.g., slitting, cutting, die-cutting, perforating and folding). The principles of these technologies and the required equipment are also described.

Chapter 11 of this book discusses advances in pressure-sensitive adhesives based on polyurethanes.

This book serves as a practical aid to manufacturers, converters, and those involved in the design and use of PSAs.

We were pleased to see the participation of scientists and industrial experts in very different areas of the field working on this book. We thank our contributors for their efforts.

The Editors

Editors

István Benedek is an industrial consultant based in Wuppertal, Germany. After exploring his initial interest in macromolecular science, he transferred to the plastics processing and adhesive converting industry as research and development manager, where he has worked for three decades. He is the author, coauthor, or editor of several books on polymers, including *Pressure-Sensitive Adhesives Technology* (Dekker, New York, 1996), *Development and Manufacture of Pressure-Sensitive Products* (Dekker, New York, 1999), *Pressure-Sensitive Formulation* (VSP, Utrecht, the Netherlands, 2000), *Pressure-Sensitive Adhesives and Applications* (Dekker, New York, 2004), *Development in Pressure-Sensitive Products* (CRC, Boca Raton, FL, 2006), *Pressure-Sensitive Design, Theoretical Aspects* (VSP, Leiden, the Netherlands, 2006), and *Pressure-Sensitive Design and Formulation, Applications* (VSP, Leiden, the Netherlands, 2006), as well as more than 100 scientific research and technical reports, patents, and international conference papers on polymers, plastics, paper/film converting, and web finishing. He is a member of the Editorial Advisory Board of the *Journal of Adhesion Science and Technology*. Dr. Benedek received his PhD (1972) in polymer chemistry and engineering technology from Polytechnic University of Temeswar.

Mikhail M. Feldstein, one of the world's leading experts in the development of new polymeric composites with tailored performance properties that span pressure-sensitive adhesives and other materials designed for medical and pharmaceutical applications, was born in 1946 in Moscow. In 1969 he graduated with honors from M.V. Lomonosov Moscow State University, Faculty of Chemistry, and in 1972 he earned his PhD in polymer science from the same university for the investigation of polyelectrolyte complexes with ionic surfactants and lipids. His early research interests were associated with the mechanisms of the formation and molecular structure of interpolymer complexes. Since 1972 he has worked in the industry of polymers for medical usage as a developer of hydrophilic pressure-sensitive adhesives for skin application in transdermal therapeutic systems and wound dressings. He received international recognition comparatively late: his earliest contacts with colleagues beyond the borders of former Soviet Union date to 1994 only. In 1999, a famous scientist and vice president of the Russian Academy of Sciences, academician Nicolai A. Platė, invited him to join A.V. Topchiev Institute

of Petrochemical Synthesis of the Russian Academy of Sciences, one of the most well-known academic institutes in polymer science. Later that year, Feldstein established long-term and large-scale research cooperation with a leading pharmaceutical company, Corium International, Inc. (CA). In 2005, Feldstein earned his DrSc in polymer science from the A.V. Topchiev Institute of the Russian Academy of Sciences.

Since the second half of the 1990s, Feldstein has focused on the molecular origins of pressure-sensitive adhesion and the interrelationship between adhesion and other properties of polymer blends. Based on gained insight into the phenomenon of adhesion at a molecular level, he has developed the first-ever technology for obtaining numerous novel pressure-sensitive adhesives of controlled hydrophilicity and performance properties by the simple mixing of nonadhesive polymer components in certain ratios. Feldstein is the author of nearly 200 research papers, 7 book chapters, and 25 patents. He is a member of Adhesion Society and Controlled Release Society. Feldstein is also an associate editor of the *Journal of Adhesion*.

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1

Pressure-Sensitive Raw Materials

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Fundamentals of Pressure Sensitivity focuses on the fundamental aspects of pressure sensitivity and *Technology of Pressure-Sensitive Adhesives and Products* and *Applications of Pressure-Sensitive Products* are practice related. *Technology of Pressure-Sensitive Adhesives and Products* discusses the manufacturing technology of pressure-sensitive adhesives (PSAs) and products (PSPs), including their chemical basis (raw materials) and engineering technology. *Applications of Pressure-Sensitive Products* describes the application domains and end-use technology of the main PSPs.

Special raw materials allow the design, formulation, and manufacture of PSAs and PSPs. Their chemical basis was described in detail in our previous works [1–4]. The fundamentals of pressure sensitivity, based on this chemical and macromolecular basis, were discussed in *Fundamentals of Pressure Sensitivity* according to the most important features of adhesive science. Interfacial and rheologic processes as the main features of pressure sensitivity were described in *Fundamentals of Pressure Sensitivity,* Chapter 1. Viscoelastic behavior as a principal characteristic of rheology in the course

of the bonding and debonding processes was discussed in *Fundamentals of Pressure Sensitivity*, Chapter 4, and correlated to viscoelastic windows in *Fundamentals of Pressure Sensitivity*, Chapter 5. Transition zones in adhesive joints and the durability of adhesive joints are discussed in *Fundamentals of Pressure Sensitivity*, Chapters 3 and 9. The role of diffusion in adhesion and the molecular fundamentals of pressure-sensitive adhesion were first discussed by Feldstein in Ref. [5]. Now advances in this field are described by Creton in *Fundamentals of Pressure Sensitivity*, Chapter 2. Pressure sensitivity was interpreted as a material property and a process by Feldstein and Creton in Ref. [6]. They continue to evaluate progress in this field in *Fundamentals of Pressure Sensitivity,* Chapters 2 and 10. The significance of relaxation for adhesion is explained in *Fundamentals of Pressure Sensitivity,* Chapter 11.

Advances in the theory of pressure sensitivity allowed the science-based design and formulation of PSAs to replace empirics. The design and formulation of PSAs constitutes the subject of our previous works [7–9]; the manufacture of PSAs and PSPs was also described by us in detail in Refs [4,10,11]. The above references are books, that is, they are available, and they cover data from research and literature searches in the whole domain of pressure sensitivity, which is very large. It is not the aim of this treatise to repeat these data; this book presents only the essentials. Chapters 1, 8, and 10 possess a general character that allows the correlation of subjects in other special chapters in these books.

As mentioned previously, the technology of PSAs and PSPs is the subject of this book. Technology generally includes the raw materials and the manufacturing process of the products. Actual PSA technology was founded on basic knowledge in material science and engineering, as discussed in *Fundamentals of Pressure Sensitivity.* The aim of this first chapter is to serve as a short guide, which allows the systematic and detailed discussion of the advances in pressure-sensitive raw materials described by specialists in the following chapters. This is a short presentation of the chemical basis of PSAs, allowing further discussion of the details of each raw material class used in the formulation of PSAs. Although the main synthesis of pressure-sensitive raw materials (elastomers, viscoelastomers, and viscous additives) is the subject of exhaustive works specializing in macromolecular chemistry and technology, advances in the in-line manufacturing technology of PSAs (especially in the development of radiation curing and web-finishing technology) impose a basic discussion of the synthesis and manufacturing technology of pressure-sensitive raw materials. In the following sections the monomers used, the polymerization technology, the technology based on polymer analogous reactions, and the formulation of off-line manufactured PSA raw materials are described in comparison with in-line synthesis.

1.1 Off-Line and In-Line Synthesis of Pressure-Sensitive Raw Materials

The manufacture of pressure-sensitive raw materials and adhesives can be carried out off-line or in-line. As illustrated in Figure 1.1, both technological modalities include various chemical technologies. Generally, off-line synthesis yields pressure-sensitive raw materials or PSAs; in-line technology leads to simultaneous PSA and PSP manufacture.

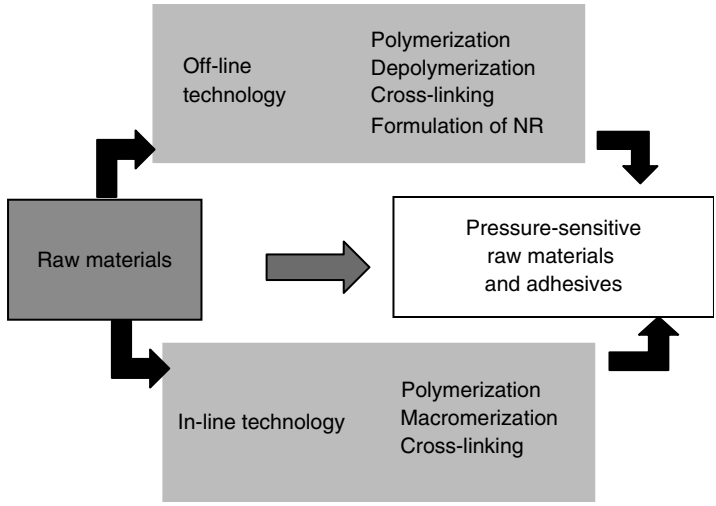


FIGURE 1.1 Principles of manufacture technology for pressure-sensitive raw materials and adhesives.

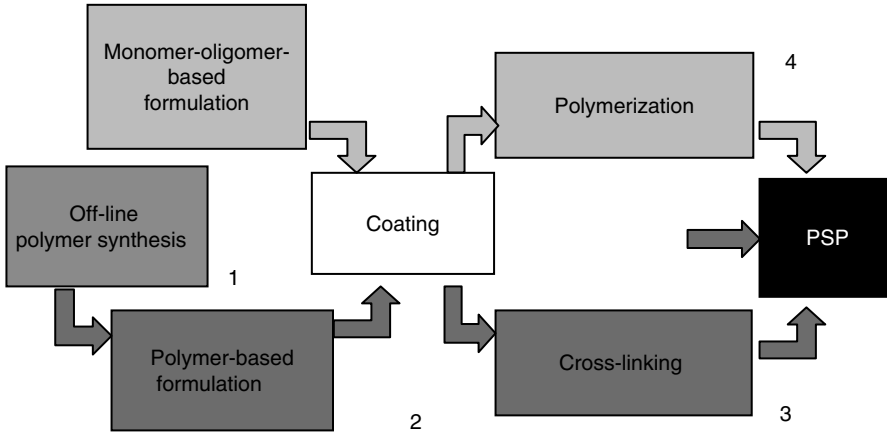


FIGURE 1.2 Manufacturing steps for PSPs.

As illustrated in Figure 1.2, off-line synthesis (1) allows polymer-based PSA formulation to be coated (2) and (if necessary) transformed (mainly by cross-linking) in PSP. Formulation is necessary because, generally, off-line synthesis yields PSA components only, that is, macromolecular raw materials that are not pressure sensitive or not pressure sensitive enough; therefore, they must be formulated, that is, mixed with other micro- or macromolecular compounds.

This is the subject of formulation. In-line manufacture of the adhesive consists of simultaneous coating and curing (3) or postpolymerization (4) of the adhesive–raw

materials. In this case, first a special "ready-to-coat" mixture of polymerizing and cross-linking monomers, oligomers, or polymers (e.g., radiation-cured hot melts) is prepared and applied on a temporary or definitive carrier material. Such a reaction mixture is transformed after coating in the ready-to-use adhesive or PSP. This post coating synthesis of the PSA must be carried out by the converter. The base polymeric raw materials for in-line synthesis are supplied by off-line synthesis. Off-line as well as an in-line synthesis was described in detail by Benedek in Refs [12,13]; therefore, the next sections provide only a summary presentation to allow the detailed discussion of the chemical basis of PSAs in the following chapters by specialized scientists.

1.1.1 Off-Line Synthesis of Pressure-Sensitive Raw Materials

Off-line synthesis of PSAs is the common way to produce PSAs. Such products can be macromolecular compounds with ready-to-use or ready-to-formulate adhesive properties or ready-to-postpolymerize reaction mixtures (monomer or polymer based), manufactured and supplied by the chemical industry to be formulated or coated in-line, that is, to convert them to a PSP. The raw materials and the technology used to transform them into macromolecular compounds with ready-to-use or ready-to-formulate pressure sensitivity are the main parameters of off-line synthesis. Owing to the wide use of synthetic elastomers domains other than that of PSAs and to the existence of a sophisticated chemical synthesis–technology, off-line synthesis, that is, the manufacture of macromolecular compounds by polymer specialists, remains the decisive part of the production of pressure-sensitive materials. The raw materials and the technology used for them are the main parameters of off-line synthesis. Table 1.1 presents the main raw materials (monomers, oligomers, polymers, and additives) for off-line- and in-line synthesis of PSAs.

TABLE 1.1 Main Raw Materials for Off-Line and In-Line Synthesis of PSAs

Raw Materials			For Off-Line Synthesis	Grade	For In-Line Synthesis
Monomers	Common	Monofunctional	•	Vinyl	•
			•	Acrylic	•
		Polyfunctional	•	Diene	—
			•	Vinyl	•
			•	Acrylic	•
	Special		—	Photosensitive	•
Oligomers	Common		—	Acrylic	•
	Special		—	Photosensitive	•
Polymers	Common		—	Acrylic, diene	•
	Special		—	Photosensitive	•
Additives	Cross-linking agents		•	Inorganic	•
			•	Organic	•
				Photoinitiators	•
	Technological additives		•	Surfactants	•
			•	Thickeners	•
			•	Stabilizers	•
			•	Solvents	•

1.1.1.1 Raw Materials for Off-Line Synthesis

The raw materials for PSA synthesis as a function of the advances in macromolecular chemistry were discussed in detail by Benedek in a previous book [14]. The glass transition temperature (T_g) and modulus of elasticity as the main parameters of pressure-sensitive design and formulation, as a function of the macromolecular characteristics (i.e., molecular weight and its distribution, comonomer content, molecular structure, sequence length and distribution, compatibility, cohesive strength/free-volume-balance, etc.), were described by Benedek in Ref. [15]. The T_g and the modulus are the main rheologic parameters of pressure-sensitive materials. As illustrated by the examples given in Table 1.2, regulation of the glass transition temperature during polymer synthesis and by formulation of the same polymers allows the decisive changes in rheology that permit use if the materials in quite different applications, for example, as a "soft" PSA or as a "hard" carrier material for PSAs. Owing to continuously increasing requirements in the end use of PSPs, especially in labeling, the values of T_g for common PSAs have changed as a function of raw material development. Some years ago, a typical PSA had a T_g of about −40°C; in fact, common acrylic PSAs possess a T_g range of −40 to −60°C.

Although polymerization and polymer analogous reactions remain the main modalities for off-line synthesis, recent advances in macromolecular chemistry allowed the synthesis of PSAs by simultaneous cross-linking and tackification, leading to hydrophilic, biocompatible polymers [5,6,16] (see also *Fundamentals of Pressure Sensitivity,* Chapter 10, and Chapter 7 in this book).

Monomers are the most important raw materials for polymerization and polymer modification. The choice of monomers, polymerization procedure, and additives decisively affects the performance characteristics of the PSA [14].

1.1.1.1.1 Monomers for Off-Line Synthesis

The most important (vinyl and acrylic) monomers for macromolecular compounds used for PSAs were discussed in detail by Benedek in Refs [13,14], taking into account their polarity and functionality, as well as their influence on the physical and chemical properties of the polymer. Advances in the use of the main monomers are discussed by Hu and Paul in Chapter 3 (monomers for block copolymers), by Willenbacher and Lebedeva in Chapter 4 (monomers for isobutene-based polymers), by Foreman in Chapter 5 (acrylic monomers), by Lin in Chapter 6 (monomers for silicone-based adhesives), and by Jones

TABLE 1.2 Glass Transition Temperature Values for Some Base Polymers and Their Use for Different PSP Constituents

Polymer	Glass Transition Temperature (°C)	Application
Polyvinyl chloride, plasticized	−40–0	Carrier, PSA
Polyvinyl chloride	+75–+105	Carrier
Poly(ethylene–VAc)	−10–+15	PSA, carrier
PP	−11	Carrier
PP, amorphous	−14	PSA

and Schmidt in Chapter 9 (monomers for silicone-based release materials). The main classes of monomers (e.g., softening, hardening, polar, and reactive compounds), the influence of carboxy functionality on adhesion, cohesion, cross-linking, and dispersion stability of the PSA, the built-in cross-linkable functional groups, hydrophilic monomers for water-soluble compositions, stabilizing hydrophilic comonomers, and some special comonomers were also described by Benedek in Refs [13,14], where screening formulations for synthesis of water-based acrylic PSAs were also provided and the influence of the choice of comonomers on polymer properties as well as on the properties of the dispersed polymeric system were investigated. The choice of special monomers used for water-soluble acrylic PSAs and the influence of chain length, chain branching, and monomer polarity on adhesive performance characteristics was investigated by Czech [17]. A global view of the parameters of molecular construction of PSPs was given by Benedek in Ref. [4], where the macromolecular basis (monomers, molecular weight, branching, etc.) for PSAs, as well as for the carrier material for PSPs, was described in detail.

The choice of monomers imposes the polymerization procedure (i.e., free-radical, ionic, etc., mechanism), and technology (i.e., solvent-based, water-based, etc.) affects the choice of additives, which influences the polymerization technology and rate of polymerization, the dispersion properties (e.g., particle size, stability and viscosity, and polymer properties) and determines the adhesive and end-use properties of the pressure-sensitive raw materials and the PSA. Special formulations (monomers and additives) are required for removability, water solubility/resistance, and other special properties (see also Chapter 8). Copolymerization of polyalkylacrylates with hydrophilic monomers to improve hydrophilicity is described by Feldstein, Singh, and Cleary in Chapter 7. Advances in free-radical polymerization are discussed by Hu and Paul in Chapter 3.

1.1.1.1.2 Additives for Off-Line Synthesis

Off-line synthesis supplies elastomers with or without self-adhesivity, pressure-sensitive viscoelastomers, and viscous components used to impart pressure sensitivity to the elastomers or to improve (regulate) pressure sensitivity. Such compounds can be considered special additives. Tackifiers and plasticizers used as viscous components to impart and regulate the adhesive properties will also be described by Benedek in Chapter 8. The special aspects of the tackification of block copolymers are discussed by Hu and Paul in Chapter 3. Other micromolecular, chemical, and technological additives are included in PSA raw materials during their synthesis. Chemical stabilizing agents (e.g., antioxidants, UV-protecting agents, etc.), and physical stabilizing agents (surface active agents, protective colloids, solubilizers, etc.) are included as well. Such compounds are used as postsynthesis formulating components for PSAs (see Chapter 8).

1.1.1.2 Technology of Off-Line Synthesis

Off-line synthesis is carried out by polymerization or polymer-analogous reactions [12,13]; it also includes the off-line modification of the synthesized polymers by chemical reactions (e.g., grafting, cross-linking, and depolymerization) and, in part, physical procedures (see formulation by mixing in Chapter 8). Thus, in some cases ready-to-use (i.e., ready-to-coat) PSAs are manufactured and do not need further formulation (see Chapter 8); in other cases, adhesive formulation is imposed by technological or

TABLE 1.3 Processing Steps, Materials, and Manufacturers for Off-Line and In-Line Synthesis of PSAs

	Off-Line Formulation		In-Line Formulation	
Processing Steps	Nonreactive Base Polymer	Reactive Base Polymer and Oligomer	Polymer Synthesis	Polymer Modification
Raw materials	Monomers Technological additives	Monomers Chemical additives Technological additives	Monomers Oligomers Chemical additives Technological additives	Monomers Reactive polymers Chemical additives Technological additives
Common products	Common AC, EVAc, SBC-based PSA raw materials	Cross-linkable AC, CSBR, SBC-based PSA raw materials, reactive oligomers; macromers	PSA/PSP	PSA/PSP
Manufacturer	Chemical industry	Chemical industry	Converter	Converter

end-use requirements [18] (see Chapter 8). Therefore, the technology for off-line synthesis must cover polymer modification by grafting, cross-linking, depolymerization, and (partially) formulation as well (see also Chapter 3). Table 1.3 illustrates the various steps of the manufacture of PSAs (and PSPs) carried out off-line or in-line by the chemical industry or by converters. Polymer synthesis and the technology of off-line synthesis are described by Foreman in Chapter 5.

As can be seen from Table 1.3, with the exception of polymerization of the base raw materials, the other manufacturing steps can be and generally are carried out by converters. A special domain of off-line synthesis focuses on the manufacture of radiation-curable PSA raw materials. The preparation and adhesion performances of UV-curable acrylic PSAs were investigated recently by Kim and coworkers [19,20]. Off-line synthesis of styrene–butadiene–rubber (SBR) copolymers is described by Martin-Martinez in Chapter 2.

Polymerization in an extruder is a special off-line polymerization technology [21] that can be used, for instance, for the manufacture of water-soluble solvent-based acrylic PSAs (see also Chapter 8) that can be UV-light cured in-line. Polymerization in an extruder is a common technology for grafting and can be combined with simultaneous depolymerization in the extruder [22]. The influence of screw speed, acrylic acid and starter amount, and the cross-linking after extrusion polymerization of acrylics were discussed in Ref. [21].

As mentioned previously, a new possibility for obtaining plastomer-based PSAs is given by the manufacture of pressure-sensitive hydrogels [5,6,16]. First discovered as a special case of pressure sensitivity, the *N*-vinyl pyrrolidone–polyethylene glycol (PEG)-based aqueous blends allowed the synthesis of other PSAs and the reformulation of the theory of pressure sensitivity. As noted by Feldstein and colleagues [23], the general

applicability of the polyvinyl pyrrolidone (PVP)–PEG model to other hydrophilic polymers and plasticizers follows from the fact that the T_g of PVP-PEG system obeys fairly well Kovács's equation concerning the additivity of T_g. This equation establishes the additional criteria of adhesive capability of a hydrophilic polymer blend, which relates mainly to the physical properties of the plasticizer. Consequently, by mixing the PEG with various complementary high-T_g polymers, similar T_g composition behavior will be obtained, which accounts for adhesion. In *Fundamentals of Pressure Sensitivity,* Chapter 11, based on the analysis of peel force in the work of viscoelastic deformation of adhesive film up to break under uniaxial drawing, peel resistance is presented as a function of the self-diffusion coefficient, relaxation time, and the cohesive strength of the adhesive polymer. The physical meaning of the derived relationship demonstrates the energy of intermolecular cohesion and free volume as a factor that controls adhesion. The relationships explains why PSAs must be in a viscoelastic state. In Chapter 7 the practice of such hydrophilic polymers is described. At a molecular level, pressure-sensitive adhesion of polymer materials requires a balance between a large value of cohesion energy and a large free volume. This fundamental factor underlies the Corplex™ technology for the development of new adhesive materials by blending nonadhesive polymer components. In Corplex adhesives the high cohesion energy results from the formation of either hydrogen or electrostatic bonds between functional groups of two complementary polymer chains (noncovalent cross-linking of the polymers in the blend). The large free volume results from either the location of the reacting functional groups at the ends of the oligomer chains or the plasticization of the interpolymer complex.

Advances in the synthesis of thermoplastic elastomers will be summarized in this chapter and discussed in detail in *Fundamentals of Pressure Sensitivity,* Chapter 3, by Hu and Paul.

Principally, off-line synthesis of PSA raw materials presents advantages in comparison to in-line synthesis in that various polymerization technologies (i.e., batch, continuous; water based, solvent based, or 100% solids) with different feed-in modalities of the reaction components and various temperature and hydrodynamic conditions are possible. Feed-in possibilities include tackification during polymerization. As demonstrated, the properties of the polymers synthesized may strongly differ according to such technological changes. For instance, emulsion polymerization of acrylates carried out to complete conversion produces significant amounts of microgels; thus, full conversion must be avoided. Emulsion and suspension polymerization yield different PSA raw materials as a function of the particle size. Carboxylated SBR latexes consist of a mixture of polymer species with linear chains, branched chains, and cross-linked materials. The relative ratio of the species can be controlled by changing the concentration of molecular weight regulators and by varying factors such as conversion, reaction temperature, or polymer particle number. The critical soft monomer (EHA) level in acrylics, which affects failure nature, depends on the polymerization process. The above-listed examples illustrate the importance of the polymerization technology.

In the past decade the solution polymerization of acrylics in recovered solvents to prepare in-line radiation-curable polymers has gained special importance [24].

It is not the aim of this book to discuss polymerization technology; however, in Chapters 2–9, which describe in a detailed manner the main raw materials for PSAs,

the technological aspects of their synthesis and processing (which decisively affect their properties) will be discussed as well. Formulation of off-line synthesized pressure-sensitive raw materials will be discussed in Chapter 8. Polymer analogous reactions (e.g., cross-linking) on off-line synthesized PSA raw materials will also be described (see Chapter 8).

1.1.2 In-Line Synthesis of Pressure-Sensitive Raw Materials

Generally, for the PSA converter the manufacture of the adhesive consists of its formulation, that is, of mixing macromolecular compounds and additives. In certain cases it would be desirable for the adhesive converter to carry out its own polymerization. Such necessity appears for low-volume special products or for adhesives for which formulation is based on the mixing of low-molecular-weight products, oligomers, or prepolymers, and the converting technology of this mixture must supply simultaneously the PSA and the PSP (see Table 1.3). There are also some special cases where the formulation is made to allow the modification of the coated adhesive by postpolymerization. In this case, the last production step of the adhesive, that is, of the off-line synthesis, is an in-line process and represents the simultaneous manufacture of the PSA and PSP. The full or partial postmanufacturing of the PSA is the result of chemical development induced by the trend of solvent-free fabrication. Such formulations with 100% solids include hot melts or radiation-curable reaction mixtures. In-line polymerization, which includes polymerization *in situ* or postpolymerization, uses special multifunctional monomers or macromers and classic (chemical) or physicochemical polymerization techniques [13]. Polyaddition, polycondensation, or cross-linking is carried out.

Postapplication cross-linking can be considered a special case of off-line synthesis (finishing) of an adhesive. It is proposed to improve shear or to ensure delamination (detachment) after use. Such postcross-linking is achieved using thermal, free radical, or photoinitiated reactions.

Generally, in-line synthesis is based on polymer analogous reactions (which include functionalization and cross-linking of polymers), polymerization, and macromerization [13]. Polymerization can also be limited to the surface of an existing base polymer. Improvement of the reversible work of adhesion can be achieved by grafting polar groups onto the polymer. Surface-treatment procedures also cause polymer analogous reactions (see Chapter 10). Cross-linking required to increase molecular weight and to shift the adhesion–cohesion balance can be carried out through classic, thermally initiated reactions or by radiation-induced reactions (see Section 1.2.2).

1.1.2.1 Raw Materials for In-Line Synthesis

The raw materials for in-line synthesis are monomers or prepolymerized compounds that must be postpolymerized. As illustrated in Figure 1.3, monomer-based off-line synthesis can lead to oligomers or polymers. In-line synthesis can also use monomers as starting materials (this is the old, so-called "syrup" technology, which employs low-viscosity, reactive, and diluting monomers), but oligomer–monomer blends can also be used (in the modified syrup technology) or pure, medium-viscosity oligomers/macromers can

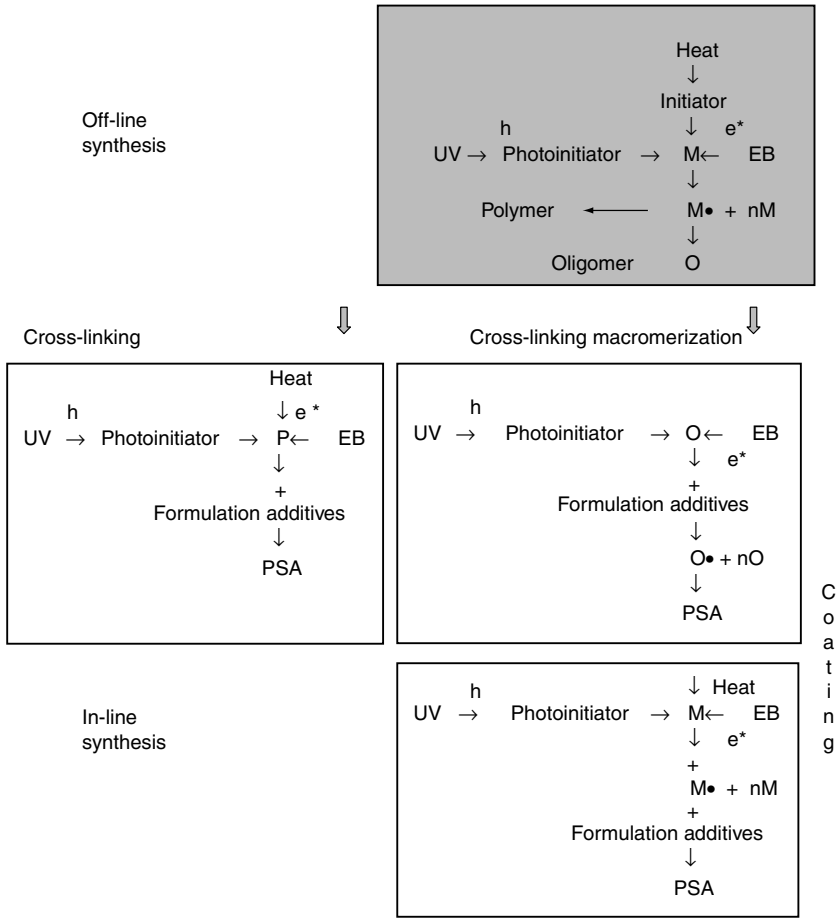


FIGURE 1.3 In-line and off-line synthesis.

be cross-linked and, finally, reactive high polymers [e.g., cross-linkable acrylics, styrene block copolymers (SBCs), etc.] can also be coated and cured.

The materials used for postpolymerization are common PSAs, PSAs with unbalanced adhesive properties, or nonadhesive oligomers. Such compounds are manufactured by off-line synthesis. Generally, they include macromolecular compounds with a low to medium molecular weight and residual functionality, that is, they can be postpolymerized (or cross-linked). For this process the converter can choose to use either a classic polymerization technology (i.e., thermal, free radical-initiated polymerization, polyaddition, or polycondensation) or a radiation-induced reaction. In some cases this choice is limited by the chemical nature of the (pre)polymer. In certain cases (i.e., acrylic hot-melt development) postpolymerization of an oligomer is a necessity because of the lack of suitable macromolecular compounds (see also Chapter 5).

1.1.2.1.1 Monomers for In-Line Synthesis

In the case of in-line synthesis, the common range of monomers (used for off-line synthesis also) is enlarged by special, radiation-polymerizable monomers and copolymerizable photoinitiators. Raw materials (e.g., monomers and oligomers) for in-line synthesis (radiation-induced polymerization and curing) were described in detail by Benedek in Ref. [24] (see also Chapter 8).

Photoinitiators were described in detail by Do and Kim in Ref. [20]. Generally, they are ethene-unsaturated, ultraviolet (UV)-reactive, functionalized, acrylated, vinylated, allylated, acrylamidated, or vinyloxidated chromophores. Photoinitiators suitable for addition are another new group of compounds with a conventional chemical group on one side, which tends to addition reaction or another kind of reaction with the carboxyl or hydroxyl groups of the polymer chain, and other photoreactive side groups. Oligomeric and polymeric photoinitiators have been developed as well. They do not show yellowing, have less odor, do not migrate, and exhibit low irritancy [13]. Although the classic way is to use external photoinitiators (e.g., benzophenone), built-in, monoethylenically unsaturated aromatic ketones can also be used for radiation cross-linking of polyacrylates. For instance, such a copolymerized photoinitiator can be an acrylic ester with benzophenone terminal groups. The built-in cross-linker makes it unnecessary for the viscoelastomer to contain unsaturated polymerizable bonds (and, therefore, it displays improved aging properties), it does not produce skin irritation, and its UV-induced polymerization is not affected by atmospheric oxygen. Li et al. [25] describe the synthesis of benzocyclobutenone containing polymers for UV light-curable PSAs. Under UV radiation, benzocyclobutenone readily reacts with itself and also with an alcohol to produce an ester; thus, in this case UV-induced cross-linking occurs without an initiator.

Like common, off-line synthesis, photoinitiated in-line polymerization is strongly affected by the choice of monomers. However, this choice is limited because of the rheologic and technical requirements, which can be contradictory. Concerning the monomers used for radiation curing, they must fulfill different requirements for the main radiation-induced polymerization procedures, that is, the UV-light-induced and electron beam (EB)-induced polymerization. In particular, UV light-polymerizable monomers require functionalities other than EB-curing ones.

As discussed in detail by Benedek in Ref. [13], formulation for UV light-curable PSAs must allow pronounced molecular mobility. Relatively low cross-linking density and a glass transition temperature lower than $-20^{\circ}C$ are necessary to fulfill such requirements. Ethyl acrylate, butyl acrylate (BA), glycydylmethyl acrylate, and acrylic acid may be used as monomers for prepolymers. To improve the coatability of monomer-based, UV light-induced formulations, thickened monomer mixtures were proposed [20]. In this case, nonreactive or reactive oligomers can serve as thickeners. If the recipe contains reactive oligomers as well, reactive diluents are used to "dilute" them. The term *reactive diluent* generally refers to an unsaturated ethylene monomer that is miscible with the principal oligomers, which reduces the viscosity of the composition and reacts with the oligomer to form a copolymer. In some cases, the addition of the reactive diluent not only reduces the viscosity of the uncured diluent composition but also increases

the elongation of the cured coating. The polymers synthesized by UV-induced polymerization must possess an elastic network. Therefore, the reaction mixture contains multifunctional monomers as well. The main common multifunctional (cross-linking) monomers and diluting monomers, as well as their influence on the properties of the PSA, were described in detail in Ref. [13]. To improve the coatability of monomer-based, UV light-induced formulations, thickened monomer mixtures were proposed [20]. The difficulties encountered in the use of UV-light or EB-curable systems are similar: high viscosities, air inhibition, and potential pollution from volatile monomers.

The EB is a much higher energy source than UV light and promotes a higher level of cross-linking, so UV light-curable formulations cannot be used unchanged for EB. EB-induced polymerization requires unsaturation; therefore, certain UV-curable formulations are not adequate for EB curing. EB curing supposes the reaction of a vinyl unsaturation with the electrons of suitable energy levels. For instance, 1,2-polybutadiene requires a high radiation dosage for cross-linking. The curing occurs more easily if acrylates are added in the formulation. Better results are obtained with hydroxylated or epoxidized acrylics as curing sites together with ethylhexyl acrylate (EHA) as a monomer. EB-cured formulations are composed of oligomers, prepolymers (50–100%), multifunctional monomers, and additives, or they are based on polymers. In the case of EB-induced curing, where a multifunctional monomer is used, its concentration should be preferably 1–5% bw (in comparison, the effect of diluting monomers used in UV light-induced polymerization is investigated at a level of about 10%). Radiation-curable SBCs are described by Paul and Hu in Chapter 3.

1.1.2.1.2 Oligomers and Macromers for In-Line Synthesis

In in-line PSA synthesis on the web, the precise regulation of the polymerization (or curing) as a function of the adhesive raw materials, thickness of adhesive layer, and carrier characteristics is difficult. In the first stage of development (which uses monomer-based formulations), side-reaction products and effects (e.g., residues of unreacted monomers and initiators, carrier damage, etc.) created technical, environmental, and physiological problems. Additional negative technological aspects appeared. The coating of such low-viscosity fluids requires special devices (see Chapter 10). Therefore, macromerization, that is, the use of prepolymerized or polymerized raw materials (reactive oligomers or polymers), and their postpolymerization have been preferred. The polymerization techniques for UV-polymerizable PSAs from thickened monomer blends and from prepolymerized monomer mixtures are described by Do and Kim in Ref. [20]. The manufacture of UV-cross-linkable acrylates is discussed in this paper as well.

Technological reason and insufficient progress in acrylic hot melts forced the development of oligomer-based and macromer-based curable formulations. Macromerization includes the synthesis of a relatively low-molecular-weight polymer and its polymacromerization or cross-linking [13]. The use of macromers is not new. It was developed as graft copolymerization and cross-linking of plastomers. In water-based systems, adhesive modification by macromers is known as well. This method can be considered a development of the use of thickened monomer mixtures. In this case, thickening is carried out with a reactive prepolymer. In the first step, this prepolymer is either a viscous liquid or a solid that can be melted. (For instance, for filled, UV-cured self-sustaining

pressure-sensitive tapes, the monomers may be partially polymerized—prepolymerized—to a coating viscosity of 1–40 Pa · s before the microbubbles are added). In the next step, the prepolymer is blended with additives such as UV-reactive diluents, photoinitiator, and antioxidants to provide a curable PSA. The macromer (polymeric precursor) formulations start from monomer mixtures containing a hard monomer with a high glass transition temperature ($T_g > -25^oC$), a soft monomer ($T_g < -25^oC$), a tackifying monomer ($T_g < 25^oC$), and multifunctional monomers (e.g., pentaerythritol triacrylate). For instance, a mixture of acrylic acid (AA)–BA–diethyl fumarate has been polymerized to a macromer, which can be coated as a hot melt and postcross-linked using EB. Macromerization appeared as a technological need, but it also offers major formulation advantages. It is a new tool to design segregated polymer structures. The raw materials used for macromerization are discussed in detail by Benedek in Ref. [13].

The best known, classic, oligomer-based systems are the polyurethane adhesives and the solventless silicones [26] (see also Chapter 9). Light-curable, functionalized oligomers, based on polyisoprene (PI) and poly(ethene–butene) were developed. They are low-molecular-weight products with special functional groups polymerizable by cationic UV curing. For instance, the product of Shell (EKP-207) is an epoxidized mono-ol, and L-1203 is a mono-ol. Such a product has a primary functionality on one end and epoxidized PI on the other end. Its fully saturated backbone consists of poly(ethene–butene) rubber; its glass transition temperature is -53^oC. The other polymer, L-1203, is a linear poly(ethene–butene) rubber with a terminal aliphatic primary hydroxy group on one end (see also Chapter 3). Such products were recently tested as mounting adhesives in the automotive industry [27–29]. Epoxidization as method to enhance UV light-induced polymerization ability is used for silicone release as well (see Chapter 9).

The most used prepolymers are acrylates or possess acrylate units as reactive sites. Photopolymerizable radical and cationic polymerizable formulations were developed. Cationic formulations contain carboxylate oligomer, cationic photoinitiator, and a photosensibilizing agent. The free-radical polymerizable formulation is based on urethane–acrylate and contains a urethane–acrylate oligomer, acrylate monomer, ketone photoinitiator, tackifier, thickener, and antioxidant. Low-molecular-weight (less than 5,000 Da) full acrylic oligomers, diluted with reactive monomers, were synthesized in solution polymerization [13]. Based on the need for a cost-effective low-refractive-index material, a hydrogel was developed by Chang and Holguin (see *Applications of Pressure-Sensitive Products,* Chapter 3) that was easily processed and had good mechanical strength. The formulation included UV-curable PEG acrylate oligomers.

The best known macromer-based products are acrylic warm melts, postpolymerized by UV light. The development of new, low-cohesion acrylic warm melts requires postcross-linking. Therefore, the large-scale application of UV-induced postcuring is enhanced by this raw material development. Such a polymer is, before cross-linking, a highly viscous fluid (at room temperature), which can be processed at 120–140°C (common hot-melt PSAs (HMPSAs) are processed above 170°C) with a viscosity of about 10–20 Pa · s (common HMPSAs have a viscosity of 80 Pa · s); its coating technology is described in Chapter 10.

Such acrylic warm melts were BA acrylate, vinyl acetate (VAc), AA, etc.) with a small amount of UV-reactive comonomer (e.g., unsaturated benzophenone derivative) and

with varying contents of 2-hydroxyethyl methacrylate [13]. The photoreactive, solvent-free acrylic PSA is made by a one-pot, two-step reaction that eliminates the gelation problems. Monomers are polymerized by solution techniques to form a high-solids (50–80%) acrylic elastomer. AA or hydroxyalkyl acrylate are used as functional monomers. After polymerization the chain is further functionalized with pendant double bonds, and the pendant hydroxyls are reacted with allyl isocyanate, maleic anhydride, 3-aminopropyl vinyl ether, or 1-(2-isocyanato-1-methylethyl)-3-(1-methylethyl) pentene or by incorporation in the polymer backbone of an unsaturated photoinitiator. Photoreactivity adjustment of the acrylic PSA is achieved by polymerization of unsaturated or additionable photoinitiator with a double bond suitable for polymerization that builds a UV-polymerizable compound with spacers and chromophoric parts, or is polyadditioned on reactive chemical groups (e.g., COOH, OH). Such compound with spacers and chromophoric parts is photopolymerizable [30].

The manufacture and performance characteristics of UV-cross-linkable acrylic hot melts with built-in photoinitiators are discussed in detail by Do and Kim in Ref. [20]. Such monomer-free and double-bond-free acrylic polymers do not cause skin irritation, so they can be used for medical applications (see *Applications of Pressure-Sensitive Products,* Chapter 4). In the future, macromerization may be used on a large scale. Typical representatives of radiation-curable oligomers and polymers are listed in Table 1.4.

UV light-cross-linkable PSAs and UV light-polymerizable PSAs were investigated comparatively by Do and Kim [20]. Improved curing ability of SBCs was achieved by functionalization of the mid-diene sequence and a mercaptopropionate derivative.

TABLE 1.4 Oligomers and Polymers Used for Radiation-Induced In-Line PSA Synthesis

Chemical Composition	Reactivity	Commercial Name	Viscosity (Pa · s)	Processing Temperature (°C)
Acrylic oligomer	UV curable	Acronal DS 3429	10–20	120–140
Polyurethane acrylate oligomer	UV curable	—	10–15	120
Polyester-acrylate oligomer	UV curable	—	2–10	100
	EB curable			
Poly(ethylene–butene) functionalized oligomer	UV curable	—	20	100
Styrene block copolymer	UV curable	Kraton LLC	5–80	175
		EKP-200, L-1203		
Epoxidized block copolymer	UV curable	Kraton EKP 207	80	175
SIS star block copolymer	UV curable	Kraton 1320X	70	175
	EB curable			
Styrene–butadiene–styrene radial block copolymer	UV curable	Kraton KX-222C	60	175
	EB curable			

A complex cross-linking system for an optically clear PSA used as a mounting aid in electronics, which includes various mechanisms, is described by Chang and Holguin in *Applications of Pressure-Sensitive Products,* Chapter 3. Using different chemistries and curing processes, an optically clear adhesive was developed for the needed complex transition from a removable PSA to a permanent PSA and, finally, a structural adhesive for this application. The first stage of product manufacturing utilized ionic cross-linking of the acrylic polymer during the coating and drying phase. The second stage used UV curing for cross-linking the urethane oligomer, which forms an interpenetrating network, and the third stage used thermal curing to completely cross-link the acrylic polymer. Such a typical, curable PSA blend has the following composition: 70.0 pts acrylic PSA (dry weight basis), 30.0 pts aliphatic urethane diacrylate, 1.4 pts benzophenone (photoinitiator), 1.4 pts methdiethanolamine (photoinitiator), 0.6 pts aluminum acetyl-acetonate metal chelate ionic cross-linker, and 0.6 pts methacrylated silane cross-linker.

The formulation of radiation-curable adhesive compositions is discussed in Chapter 8. Foreman et al. used a saturated hydrocarbon macromer [e.g., poly(ethylene–butylene) methacrylate], to create a grafted acrylic–rubber PSA. The rubber phase is compatible with hydrocarbon resins, including fully saturated resins (see Chapter 5).

1.1.2.2 Technology of In-Line Synthesis

Based on the experience of radiation curing of thin coatings from printing technology, in-line coating and polymerization of the base monomers (actually of a blend of monomers, oligomers, and reactive diluting agents) were carried out to manufacture PSA-coated laminates. The main problems with this (syrup) technology had to do with chemistry, physiology, and rheology. Later, polymerization (with nonreactive polymers) of thickened reaction mixtures was developed. In the next step, advances in macromolecular chemistry allowed macromerization, that is, polymerization of oligomers (mixed with reactive monomers or pure). Thus, radiation-curable warm melts (i.e., polymers with a low softening point and viscosity) and hot melts were manufactured. Their manufacture technology as a high-solids-content polymer solutions is described by Benedek in Ref. [24]. Their manufacture technology in an extruder, followed by postcoating, radiation-induced polymerization, is discussed by Czech in Ref. [17]. In a different manner from off-line synthesis, which generally leads to pressure-sensitive raw materials, that is, compounds that must be transformed in a finished PSA by the formulator (except ready-to-use products), in-line synthesis must produce a finished PSA or a finished PSP. Therefore, in this case, formulation is included in polymer synthesis, and formulating additives may interact with the components of the polymerization recipe.

Adhesive formulations for UV light-induced curing and EB curing were developed (see also Chapter 8). The polymerization conditions for UV light-induced and EB-initiated curing are quite different. The UV light-induced photopolymerization of acrylics uses 280–350 nm light, with an intensity of 4 mw/cm^2 at the surface. The efficacy of UV curing depends on the emission spectrum of the UV lamp, the photoinitiator (its absorption in the emission domain of the lamp), and the transmittance of the UV light-cured layer. The length of polymerization zones and the density of lamps in these zones affect the manufacturing process. Because of the relatively low energy density, the maximum web

width and running speed of UV-curing lines is limited. Cooling is provided by low-temperature nitrogen gas. The chamber has an atmosphere of nitrogen. Inerting with nitrogen is of no benefit for cationic UV light-induced polymerization, where humidity hinders cross-linking. Although inertization costs about 0.001–0.002 €/m^2, inertized UV light systems are preferred because they allow a polymerization yield of 95%. A UV light-curing device is the easiest to add to existing equipment. The capital costs for UV lamps are much lower than for thermal systems and, compared with thermal curing systems, UV systems demand only 1% of the energy consumption. Technological details (equipment) of the UV light-curing system are described in Refs [13,31] and in Chapter 10. The mechanism of UV light-induced photopolymerization and the cross-linking agents and photoinitiators used were described in detail in Refs [13,20,31]. For common PSPs, a comparison of UV-curing displays with EB (and thermal) curing resulted in the following disadvantages: rough paper surfaces are unsuitable and curing is insufficient and not applicable for laminates. Because the adhesive layer absorbs radiation , UV-curable products must have a limited coating weight.

EB curing has the advantage of high coating weights (50–80 g/m^2). For pigmented layers it can use a coating weight of 300 g/cm^2, compared with 50–80 g/m^2 for UV light-cured systems. UV light-induced curing allows running speeds of 100–200 m/min in comparison to EB-curing lines, at 100–500 m/min. Ozone formation must be avoided by nitrogen injection or by exhausting. EB-induced curing is color blind and dries all compositions with the same speed. It can cure thick films, even through opaque surfaces, but it must operate in a sealed, pressurized chamber using nitrogen or carbon dioxide. Low and no inert gas curing were developed [24]. Hybrid systems with combined UV light/EB or hot air/EB were developed as well [13]. UV/EB cure mechanisms are also used with silicone PSAs, with the advantages of much lower energy requirements and a smaller equipment footprint. Two recent patents describe the use of UV/EB cure with and without thermal activation of the initiator [26]. A silicone PSA composition that uses a thermal/UV dual-cure mechanism to leverage the benefits of UV cure and the properties of thermal-cured silicone PSAs have been described [32]. A comparative examination of UV-induced and EB curing is given in Table 1.5.

1.2 Basic Products for Pressure-Sensitive Adhesives

In their first stage of development PSAs were formulated on the basis of natural macromolecular products. Natural rubber (NR) and natural resins were used. Some decades ago, synthetic elastic components (rubbers) and viscous raw materials (tackifiers, plasticizers, etc.) were developed and blended to produce (formulate) the adhesive. Advances in macromolecular chemistry allowed the synthesis of raw materials with built-in viscoelastic properties, that is, pressure sensitivity [e.g., acrylics, VAc copolymers, carboxylated rubber, polyvinyl ethers (PVEs), polyurethanes (PURs), polyesters, etc.]. Some polymers used for PSAs are raw materials for other adhesives or plastics. Their synthesis involves a special chemical/macromolecular technology. It is not the aim of this book to describe the technology. The main basic products used for pressure-sensitive formulation, that is, the elastomers (random, alternative, and block

TABLE.1.5 Advantages and Disadvantages of UV Light- and EB-Induced Curing

UV Light-Cured Systems	EB-Cured Systems
Advantages	
Nonexpensive equipment	Adequate for most common PSAs with low cross-linking density and $T_g \leq -20°C$ Color blind
Disadvantages	
Need for reactive sites	Need for vinyl unsaturation
Need for photoinitiator or built-in photosensitive site	—
Need for special tackifier resins	—
Need for special stabilizers	—
For monomer-based formulations, need for thickeners	—
For monomer-oligomer based formulation, need for diluting monomers	—
Need for cross-linking monomers 10% bw	For improved efficacy, need for cross-linking monomers 1–5% bw
Limited running speed	Expensive equipment
Limited coating weight	Carrier damage
Anisotropy of the cured PSA layer	—
UV transparency required	—
Oxygen or humidity-sensitive, inerting required	Sealed, pressurized chamber required
Low-energy consumption compared with thermal curing	—
Rough paper surface inadequate	—
Not usable for laminate	—

copolymers) and the viscoelastomers (e.g., acrylics, VAc copolymers, and other vinyl polymers) are briefly presented here, allowing their detailed discussion in Chapters 2 through 8, a description of the role of PSA formulation based on these raw materials (Chapter 8), tackifiers and tackification (Chapters 8 and 3), and the manufacture of PSAs and PSPs (Chapter 10).

1.2.1 Elastomers

As discussed in detail in Refs [33–35], PSAs are characterized by special rheology and viscoelasticity (see also *Fundamentals of Pressure Sensitivity,* Chapter 4). Therefore, their first raw materials were natural and synthetic compounds that display elasticity, that is, their existent elastic network must only be "softened" to achieve pressure sensitivity. NR and some diene-based homopolymers or random and alternative copolymers are such materials. PSAs on a different chemical basis were examined comparatively by Benedek in Ref. [36], rubber-based adhesives were evaluated in comparison to acrylics, and acrylics were examined in comparison to other synthetic polymer-based elastomers. In a similar manner, Chapter 2 deals with the specific aspects of rubber-based adhesives, taking into account the advances in this domain.

1.2.1.1 Common Rubber-Based Adhesives

Natural rubber-based PSAs were the first self-adhesive products used for the manufacture of PSPs. Although NR is self-adhesive, most elastomers must be transformed into viscoelastomers to display usable pressure sensitivity (i.e., they must be tackified). The special structure of common elastomers, consisting of their high, so-called rubber-like elasticity, which is related to their partially cross-linked structure allowing strain hardening, offers a large range of modalities (tackification, plasticization, cross-linking, filling, etc.) for their formulation [13]. NR and elastomers based on homopolymers and random and alternative copolymers [e.g., diene homo- and copolymers and polyisobutene (PIB)] are the main representatives of this raw material class. NR as a base elastomer for rubber–resin PSAs is described in Chapter 2 by Martin-Martinez. Although they have a molecular structure that imitates NR, stereoregulated synthetic elastomers have only a limited use for PSAs. Screening formulations with such polymers are listed by Benedek in Ref. [13]. Styrene–diene copolymers are discussed in Chapter 2 by Martin-Martinez.

Later, thermoplastic elastomers were developed that are rubber-like and plastic-like polymers. Such so-called thermoplastic elastomers (TPEs) have a partially cross-linked structure like common elastomers, which imparts elasticity. These new, segregated, block copolymer-based thermoplastic elastomers must imitate the multiphase construction and the elastic behavior of NR. In this case, the partially cross-linked structure (segregation) is based on physical, thermally instable bonding, which allows the thermal, plastic-like processing of such elastomers. The first thermoplastic elastomers were based on styrene–diene copolymers. Advances in macromolecular chemistry and technology allowed the synthesis of a broad range of TPEs based on other monomers and with quite different build-up.

Thermoplastic elastomers were discussed in detail in Refs [4,13,25,37]. Advances in their domain will be described by Hu and Paul in Chapter 3, in which distinctive features of the mechanical and adhesive properties of styrene–diene-based block copolymers are considered compared with the properties of PSAs of others classes. The synthesis methods of styrene–diene block copolymers with different (e.g., linear, radial, tapered, etc.) structures are described; star polymers and oligomer-modified star polymers and multiblock polymers are examined in comparison to olefin- and acrylate-based block copolymers. Their tackification, based on selective compatibility, is also investigated (see also Chapter 8). The features of block copolymers, that is, their mechanical properties (e.g., tensile strength, creep, etc.), and their adhesive properties (tack, peel resistance, and shear resistance) are also investigated. Processing and limitations in the use of TPEs are also discussed. The viscoelastic properties and adhesive performance of special block copolymers and their blends [e.g., styrene–isoprene–styrene (SIS) + styrene–isoprene (SI), SISI, SI4 + SI] are examined in *Fundamentals of Pressure Sensitivity,* Chapter 5, by Chang.

In the range of elastomer-based PSPs, PIB-related PSAs constitute a special class with an old and large application field. Owing to their classic synthesis, which allows the manufacture of various, well-characterized products ranging from liquids to solids, they were used for tapes in different end-use domains (see *Applications of Pressure-Sensitive Products,* Chapter 4). Owing to their systematic investigation (including the means of

macromolecular chemistry, physics, and contact mechanics), their application performance characteristics can be easily related to their fundamental aspects, that is, they serve as model compounds. Chapter 4 discusses the fundamentals and special properties of PIB adhesives. The rheology, viscoelasticity, and adhesion of PIB-based PSAs are described. The formulation and use of PIB and butyl rubber-based PSAs is discussed by Martin-Martinez in Chapter 2 as well.

1.2.1.2 Special Elastomer-Based Adhesives

Elastomers based on heterocompounds (e.g., acrylics [4,13], PEs [4], PURs [4,13], and silicones [4]) are also used as raw materials for PSAs.

A comprehensive examination of the developments in silicone PSAs is given by Lin et al. in Ref. [26]. Developments in silicone PSAs are discussed in detail in Chapter 6 by Lin. As noted, liquid solventless and high-solids PSA compositions that can be applied using traditional application methods necessitate the use of lower viscosity, more highly functional silicone polymers and *MQ* resins, which are inherently stable. Thus, the use of silanol-functional, short-chain silicone polymers is largely excluded, leading developers to use additional or UV-curable silicone systems with components containing silicon-bonded hydride with silicon-bonded vinyl or silicon-bonded epoxy or acrylate functionalities. The use of short-chain fluids in PSA applications can provide adequate tack and adhesion, but leads to high-temperature stability and performance issues, which can be overcome through raw material selection or cure methodology [38–40]. Solvent-resistant silicone PSAs were also developed. Eckberg and Griswold [41] determined that tackifying *MQ* resins undergo facile reaction with fluoroalkylsilanes to provide modified *MQ* resins compatible with fluorosilicone gums. Fluorinated silicone resin and fluorosilicone gums combine to yield compositions with PSA properties similar to those of conventional silicone PSAs, with the added virtue of resisting solvent attack by hydrocarbon solvents. Noncoupled fluorosilicone PSA compositions have significantly improved solvent resistance, but inferior peel adhesion as a function of the fluoro content of the fluorosilicone gum. Coupled fluorosilicone PSAs can be prepared with peel resistance approaching that of conventional methyl silicone PSAs without sacrificing solvent resistance by proper selection of gum fluoro content and resin/gum (*R/G)* ratio. These new adhesives may be laminated to conventional silicone release liners to form pressure-sensitive constructions that can be readily packaged and dispensed. Additional details on the basics of silicone PSA synthesis can be found in Refs [42–48]. Sheridan [49] combined the properties of silicone with those of urea block copolymers to build stretchable, releasable constructions that adhere to low-energy surfaces.

The development of full acrylic countertypes of SBCs has been a long sought after goal [50]. Owing to the inherent and adjustable adhesion of acrylates, acrylate block copolymer systems are expected to perform better in terms of durability, resistance to photodegradation, heat resistance, tack, and moisture vapor transmission rate compared with SBCs. Unfortunately, common synthesis methods and polymer topology lead to high-molecular-weight polymers that are not processible as typical hot melts. In the past decade, major advances to gain control over radical polymerization have been realized. Among the new polymerization techniques, the atom transfer

radical polymerization (ATRP) stands out as a very efficient and practical method to prepare (meth)acrylic block copolymers of different architectures. Many examples of polymethacrylate–block–polyacrylate–block–polymethacrylate copolymers prepared by controlled radical polymerization exist in the literature [51]. Some work on the use of formulated acrylic block copolymers as PSAs has been published. These reports essentially deal with linear triblock copolymers based on poly(*n*-butyl acrylate) (as the central segment), prepared either by atom transfer radical polymerization or by living anionic polymerization [52–55]. Simal et al. [50] used ATRP to prepare a four-branched radial block copolymer in a one-pot, two-step synthesis. Other works used multivalent chain transfer agents [56] and living radical polymerization [57,58]. Anionic methods have the advantage of better control of polymer architecture [59] and tacticity [60,61]. Smit et al. [61] synthesized acrylic block copolymers for HMPSAs with methyl methacrylate for the hard phase and a low T_g monomer with lower polarity (e.g., butyl acrylate) for the soft phase. Such soft polymers are suggested mainly for medical use (see also *Applications of Pressure-Sensitive Products,* Chapter 4). Developments in acrylic block copolymers are described by Hu and Paul in Chapter 3.

It is well known from the practice of film- and fiber-forming acrylics that due to the associative possibility of the nitrile group in acrylonitrile and the (physically segregated) microdomains in such polymers, improved mechanical characteristics are obtained. It is astonishing that this "block forming" tendency is not yet used in the design of acrylic TPEs. Advances in elastomers and their cross-linking are discussed in Chapter 8.

Thermoplastic urethane elastomers (TPU) have become well-established commercial materials since their inception in the B.F. Goodrich research laboratories in the 1950s. Chemically, TPUs comprise essentially linear polymer primary chains that are segmented in structure. They contain alternating sequences (blocks) of low T_g (soft) segments and high T_g (hard) segments, which are joined together end to end with covalent chemical bonds. In the solid polymer the hard segments tend to associate strongly through urethane hydrogen bonding and π-electron attractions. As demonstrated above, such segregated structures (i.e., virtual cross-links of the hard segments) permit valuable thermoforming and solution applications of the tough, strong TPUs. The advantages of PUR elastomers were first used in common laminating and mounting adhesives, but in past decades PSAs were developed as well. Advances in this domain are described in Chapter 11.

1.2.2 Viscoelastomers

Polymers with built-in viscoelasticity possess a broader chemical basis for the manufacture of all adhesive classes (i.e., 100% solids, solvent-based, and water-based formulations) than pure elastomers. Some can be used as raw materials for noncoated PSP components. Of these compounds, acrylics are the most used.

Acrylics were developed as a raw material for PSA in the form of elastomers (rubbers) and viscoelastomers. Acrylic copolymers were the first class of viscoelastomers used for PSAs. Random and block copolymers have been synthesized as acrylic rubber. Both can be applied for solvent-based or HM adhesives. A wide range of acrylics is supplied as water-based dispersion. Recently, ready-to (in-line)-use acrylic oligomers were developed

(see also Section 1.1.2). Advances in polymer chemistry and technology supplied a large range of viscoelastomers that are usable as pressure-sensitive raw materials, threatening the leading position of acrylics in this domain. Acrylics are available as solvent-based, water-based, and 100% solids. They are supplied as common acrylic rubbers and thermoplastic elastomers as well. Owing to their very large monomer basis, their copolymerizability by various procedures (including in-line technology-required radiation-induced polymerization), their built-in pressure sensitivity (which can be, if necessary, easily regulated by tackification, cross-linking, etc.), and their excellent aging and physiological properties, acrylics remain the main class of pressure-sensitive raw materials. Functionalized acrylics can be used for special products. For instance, side-chain fluoroacrylate monomers such as ^{1}H,^{1}H-pentadecafluoro-octyl acrylate and ^{1}H,^{1}H-heptafluorobutyl acrylate were used together with a nonfluorinated comonomer (acrylic acid) to obtain low-refractive-index polymers (see *Applications of Pressure-Sensitive Products,* Chapter 3). UV curing of urethane diacrylate was combined with thermal curing to obtain a structural adhesive used in electronics by Chang and Holguin (see *Applications of Pressure-Sensitive Products,* Chapter 3). Advances in macromolecular synthesis led to acrylic hydrogels (based mostly on hydroxyethyl acrylate) that are curable chemically or by radiation. Their use in electronics is discussed in *Applications of Pressure-Sensitive Products,* Chapter 3, by Chan and Holguin. Acrylic hydrogels are examined in comparison with other products in Chapter 7 by Feldstein et al. In Chapter 5, Foreman describes acrylic adhesives.

VAc copolymers are the main competitors of acrylics as raw materials for viscoelastomers and elastomers [4,13]. The first trials of incorporating polar monomers in ethylene [or ethylene–vinyl acetate (EVAc)] copolymers were carried out with acrylates. Unfortunately, faster reacting acrylates (relative to ethylene or VAc) have a tendency toward block copolymerization with vinyl acetate. The disparity in the reactivity ratios between ethylene and acrylates with respect to VAc also limits ethylene incorporation into a terpolymer system. Maleates (or fumarates), on the other hand, do not readily homopolymerize, leading to alternating copolymers with vinyl acetate; this, coupled with a much more favorable reactivity toward VAc and ethylene, enables the production of terpolymers with an increased ethylene content. The two preferred comonomers among EVAc terpolymers for optimal pressure-sensitive performance are dioctyl maleate and 2-ethylhexyl acrylate (2-EHA). The higher molecular weight of dioctyl maleate allows a lower molar fraction, permitting a higher ethylene content. Thus, polymers commercialized by National Starch contain 20% or more ethylene by weight. Acrylic and ethylene copolymers may be incorporated in aqueous EHA-based PSA systems. VAc displays excellent copolymerization ability with a broad range of common and special monomers. The homopolymer of this classic monomer was used on a large scale for common non-PSAs and was the most used and investigated material in this domain. The copolymerization of VAc with nonpolar and polar comonomers (e.g., ethylene, acrylates, maleinates) leads to products with self-adhesivity (see *Applications of Pressure-Sensitive Products,* Chapter 7), which can be easily regulated by the nature and ratio of comonomers, copolymerization technology, by formulation and application conditions. Thus, VAc are used for PSPs as carrier materials, adhesives, and release materials. Like acrylics, they can lead to rubber-like as well as thermoplastic products. They are used as solvent-based, water-based, and 100% solids.

Chapter 6 describes the silicone-based PSAs as competitors of acrylics. Silicones are a class of heteropolymers that (due to the special nature of the silicone–carbon bond), display valuable application properties. They present increased thermal resistance coupled with positive physiological characteristics (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Owing to numerous chemical possibilities, various synthesis methods can be used to incorporate different monomers into polysiloxane, and due to the regulation of the organic/inorganic ratio in the polymer and other macromolecular characteristics, it was possible to fine-tune the adhesive properties, leading *ad absurdum* to nonadhesive products used as release liners (see Chapter 11). Silicone-based adhesives were described in Refs [4,15,26]. Recent advances in this domain are presented by Li in Chapter 6.

As mentioned in Section 1.1.1.2, a special class of PSAs is based on simultaneous cross-linking/plasticizing of common, non-pressure-sensitive plastomers like PVP. In this manner, hydrophilic polymers are manufactured. Hydrophilic PSAs were discussed in detail in Refs [16,62,63]. Chapter 7 describes the advances in synthesis and application of such hydrogels, including bioadhesives.

Urethane derivatives display an increased reactivity and, therefore, are used as monomers (for polymerization, polyaddition, or polycondensation) and as cross-linking agents for various classes of other pressure-sensitive raw materials [4,15,31]. Their polymers form films as well, and such films with excellent thermal and chemical resistance are used as carrier materials for PSAs [4]. PURs as adhesive raw materials were used mostly for common, lamination adhesives, as solvent-based or water-based compositions. Developments in this field allowed the synthesis of block copolymers [24]. Urethane derivatives are used as a release material for PSAs as well [64]. Advances in PUR chemistry supplied new raw materials that can be used for the formulation of PSAs. Developments in this domain are described by Czech and Hinterwaldner in Chapter 11.

1.2.3 Viscous Components

The formulation of elastomer-based or viscoelastomer-based PSAs uses viscous components for tackification. Tackier resins and plasticizers are added to the recipe. Tackifiers were described in our previous works [4,24,37]. Advances in chemistry and the use of tackifiers are discussed in Chapter 8. Tackification, especially selective tackification for segregated polymers, is discussed by Hu and Paul in Chapter 3.

1.2.4 Comparison of PSAS on a Different Chemical Basis

PSAs on a different chemical basis were compared by Benedek in Ref. [30]. Rubber-based versus acrylic-based PSAs were examined comparatively, taking into account their common and special adhesive properties and stability. Rubber–resin-based adhesives possess excellent tack and peel resistance but remain defensive in shear resistance. Table 1.6 compares the various base polymers used as PSA raw materials.

Acrylic PSAs offer a unique combination of performance advantages relative to hydrocarbon-based rubber–resin adhesives and are used extensively in end-use markets that demand excellent color and clarity, weatherability, durability, and plasticizer migration resistance. Acrylic PSAs also display better specific adhesion properties. Generally, the

TABLE 1.6 Comparative Examination of the Main PSA Raw Materials

Performance	Acrylic	EVAc	NR	SBC	SBR
Raw materials	1 Copolymerizable with various acrylic, vinyl, and diene comonomers	2 Limited copolymerization	3 Only polymer analogous reactions and depolymerization possible	4 Limited comonomer availability	3 Limited comonomer availability
Synthesis/ manufacture	1 Off-line and in-line; free-radical, ionic, etc., mechanism; thermal- and radiation-induced polymerization possible	2 High pressure required; only off-line free-radical polymerization possible	4 —	3 Limited expensive technology	4 Limited expensive technology
Formulability	1 Compatible with various base polymers and tackifiers	2 Limited compatibility	1 Compatible with various base polymers and tackifiers	4 Limited compatibility with common tackifiers; limited cross-linking ability	3 Limited compatibility with other base polymers and tackifiers
Grades					
Monomers	1	2 Limited choice	—	4 Limited choice of hard block	4 Limited choice of styrene derivative
Oligomers	1	4 No commercial product	3 Limited choice	4 Special functionalized products only	4 No commercial product
Block copolymer	4	Experimental products	—	—	—
Solvent-based	1	4	1	4	3
Water-based	1	1	1	—	1
Hot-melt PSA	4	4	4	1	—

Note: 1–4 denotes the adequacy of a base polymer to be used as a PSA raw material.

advantages of acrylic systems include chemical and water resistance, UV and oxidative stability, heat resistance, tack at varying temperatures, and the balance of adhesive and cohesive properties. As noted in Refs [17,20], acrylics are also used in special domains, such as water-soluble adhesives (for splicing tapes, bottle labels, and various medical products; see also *Applications of Pressure-Sensitive Products,* Chapter 4) or for removable adhesives. Acrylics are the most used monomers, oligomers, and polymers employed for radiation-induced in-line manufacture of PSAs and PSPs (see also Section 1.1).

Rubber–resin adhesives provide a compromise of high cohesive strength for conformance to curved substrates and good tack required in automatic labeling, but they exhibit varying batch-to-batch consistency and can cause staining problems. On the other hand, their high cohesive strength, softness, good anchorage, and high conformance make them absolutely necessary for processing-protection films (see also *Applications of Pressure-Sensitive Products,* Chapter 4). Low-energy carrier materials and soft, rubber-based PSAs bond fairly well (anchorage), but they are difficult to convert, whereas acrylics convert well, but exhibit low anchorage. Properties that are correlated with the chemical instability of a rubber–resin basis (e.g., temperature and light resistance) and the pronounced liquid character of the rubber–resin mixture (e.g., cold flow and shear sensitivity) remain inferior for rubber–resin PSAs compared with acrylic PSAs (see also *Applications of Pressure-Sensitive Products,* Chapter 8). Rubber–resin PSAs based on TPEs display inferior cuttability, resistance to migration, and thermal and UV stability in comparison with acrylics (see also Chapter 10 and *Applications of Pressure-Sensitive Products,* Chapter 8).

Acrylics were compared with other synthetic polymer-based elastomers in Ref. [36]. The tack of unformulated acrylic PSAs is lower than that of tackified, rubber-based PSAs [e.g., EVAc and carboxylated butadiene rubber (CSBR)], but higher than that of other untackified adhesives, except PVEs. Acrylics possess better tack at any coating weight level. The tack of formulated acrylics was examined taking as criterion the ease of tackification, tackifier level and tack level. Acrylics possess good overall compatibility with common tackifiers, which can be fed into as solutions or dispersions to water-based acrylics. A level of 30–40% (by wet weight) tackifier resin is commonly used for acrylics, and a tackifier level of 10–20% suffices for tack improvement of acrylic PSAs. The suggested tackifier level for PSA formulations on different chemical bases (e.g., acrylic, vinyl–acrylic, SIS, SBR, and EVAc) is discussed by Benedek in Ref. [36]. Acrylics need a lower tackifier concentration for maximum tack than CSBR or vinyl acrylics, and the tack maximum (as a function of tackifier concentration) is broader. Generally, the ease of tackification depends on the chemical composition and structure of the polymer. High-molecular-weight acrylic dispersions yield a low tackifying response. The tack level of tackified acrylic PSAs is superior to that of tackified EVAc, but lower than the tack of tackified CSBR (see also Chapter 2 and Ref. [36]).

The special features of water-based acrylic PSAs compared with other water-based PSAs were discussed in Ref. [36]. Generally, water-based acrylic PSAs possess a higher solids content and a higher solids content/viscosity ratio than common CSBR or EVAc dispersions; they also respond better to diluting. Water-based acrylic PSAs exhibit a lower surface tension than common CSBR or EVAc dispersions. On the other hand, water-based acrylics show higher coagulum (grit) than CSBR dispersions, although they display

better mechanical stability than CSBR. They generate less foam formation than CSBR and EVAc. Water-based acrylics demonstrate better wet-out properties and can be converted at higher speeds than EVAc and CSBR dispersions. Solvent-based acrylics have some special characteristics compared with classic, rubber–resin PSAs. They have a higher solids content (20–30%), and the solids content/viscosity ratio can be adjusted exactly. Generally, special solvents are used [17,21,24,36], and both solutions or dispersions can be produced. In general, if fewer or no plasticizers and antioxidants are used, cross-linking is possible. Cross-linking of acrylics was discussed in detail by Czech in Ref. [31].

As illustrated in Chapter 8, which discusses the role of formulation and the main formulation modalities, softening of the elastomers and viscoelastomers by tackification (and plasticization) and their cross-linking produce macromolecular composites. As described in Chapter 10, the manufacture of PSPs leads to laminates, which are macroscopic composites. That means that PSPs must be evaluated as heterogenous structures (systems), that is, as multiple composites. In the next section, the multiple composite build-up of PSPs as a whole will be briefly examined.

1.3 Pressure-Sensitive Products as Composites

The best known pressure-sensitive raw material (the model compound) is NR. Its build-up illustrates that an adequate balance of the plasticity and elasticity of a macromolecular compound can be achieved by a network structure. Such a network contains rigid, cross-linked parts and flexible, linear parts. The cross-linked part may suffer deformation and the non-cross-linked parts can undergo chain entangling. According to a general concept, such a network is a composite.

Principally, a composite includes a matrix and a reinforcing element. The matrix is the soft (plastic/elastic) continuum that contains a rigid (elastic/plastic) discontinuum. The flow of such a structure is ensured by the matrix; its deformation stability is the result of the interaction of the reinforcing element with the matrix. Bonding needs flow and debonding needs stability against deformation. Such deformation may be plastic or elastic, permanent or temporary.

Recent advances in PSPs lead to composites on a macromolecular level, on a macroscopic level, and on a product construction level. The influence of the composite structure on the PSA was discussed by Benedek in Ref. [33].

1.3.1 Pressure-Sensitive Products as Composites on a Macromolecular Scale

Composites on a macromolecular scale include synthesized and formulated composites. Macromolecular compounds can be built up as a composite or they can be mixed into a composite. Synthesized macromolecular composites contain (like NR) a network structure. "Mixed" macromolecular composites work like filled systems, where the rigid component acts as a filler in a soft macromolecular matrix. Generally, the range of the interchain interactions may differ and, thus, more or less tightly bonded networks are formed. In the case of synthetic macromolecular composites the polymeric network can

be the result of chemical interactions (e.g., chemically cross-linked systems) or physical interchain interactions (e.g., physical association).

As noted in Ref. [10], filled systems are special compositions, where the role of the filler can be played by various components (e.g., crystallites, polymer sequence, or fillers). Multiphase rubbery polymers can be considered elastic networks or filled systems. The stress–strain behavior of such polymers can be adequately modeled by the Mooney–Rivlin equation as an elastic network (considering the trapped entanglements as finite cross-link junctions) or using the Guth–Gold equation relating the stress level (modulus) to the hydrodynamic effects of the styrene blocks considered fillers. Thermoplastic elastomers with segregated structures can be considered filled systems (i.e., composites). They possess a segregated structure on a molecular scale. Their properties depend on their morphology, which is a function of the relative concentration of the components. The morphology of an SBC in its solid-state depends on its polystyrene content. Tackified TPE compositions can be considered diluted systems [37]. In this case the main polymer possesses a segregated composite structure that becomes a multiple composite by "dilution" with the tackifier. According to the filler theory, the polystyrene domains works as a filler dispersed in the continuous polydiene matrix. In this case, the plateau modulus G_n^0 is given a function of the density ρ, the molecular weight between entanglements M_c, and volume fraction Φ of the filler,

$$G_n^0 = (\rho/M_c)\mathrm{RT}(1 + 2.5\Phi + 14.1\Phi^2) \tag{1.1}$$

like the elasticity modulus E in the Gooth–Smallwood [65] equation.

$$E = E_0\,(1 + 2.5\Phi + 14.1\Phi^2) \tag{1.2}$$

According to Hu and Paul (see Chapter 3), the styrene hard blocks not only serve as a physical cross-linking agents, but also behave like rigid fillers in a continuous rubbery phase. Therefore, as the concentration of the hard blocks (either styrene block or the high softening point end-block tackifiers) increases, the filler content increases, and the adhesive becomes stiffer. Excessive end-block tackifier will separate from the styrene matrix and form an individual tackifier phase, acting like fillers, which could significantly increase melt viscosity and reduce adhesive tack and clarity.

The composite structure of the tackified compositions is more complex because segregation occurs in the diluted system as well. For instance, as noted by O'Brien et al. [66] by the investigation of tackified SBCs, the subsurface of the PSA demonstrates a spherical morphology characterized by glassy styrene domains in a rubbery matrix. Atomic force microscopy (AFM) images consist of white styrene domains imbedded in a multicolor matrix, suggesting that the rubbery matrix is not composed of a single phase. Rheologic evidence also supports the existence of a two-phase rubber matrix from the bimodal tan δ (see also *Applications of Pressure-Sensitive Products,* Chapter 8). The rubbery matrix is likely composed of a tackifier-rich phase and an isoprene-rich phase. O'Brien et al. observed an isoprene–resin phase (a resin-rich phase) and, surprisingly, a second phase composed mostly of isoprene (an isoprene-rich phase). Tse [67] and Class and Chu [68,69] also confirmed the presence of a shoulder at −40°C using

rheology and transmission electron microscopy in NR-based and SIS-based adhesives. However, the reasons for the existence of the third phase were not clearly explained. Except for the mid-block and end-block phases, there is an additional tackifier-rich phase in SBS tackified with hydrocarbon resins (see Chapter 3). A supramolecular ordering of spherical microdomains embedded in a continuous matrix was established by AFM for a radial acrylic block copolymer by Simal et al. [50]. Differential scanning calorimetry results also suggested that the thermoplastic microdomains are partly miscible with the tackifier. Furthermore, the radial structure of the block copolymer introduces additional chemical cross-links and, hence, produces a dense network that appreciably improves the holding power. This network provides the required cohesion for suitable adhesive performance in PSAs. In contrast, the statistical copolymer has a poor cohesive strength as a result of the low number of temporary entanglements typical for polyacrylates. A two-phase structure exists in silicone PSAs as well. A "resin-rich" phase and a "gum-rich" phase were described by Lin et al. [26]. The composite structure of tackified systems is strongly influenced by their manufacture. According to Kajiyama [70], the phase structure of PSA mixed with a tackifier in the monomer state and solution polymerized was different from that of expected from the phase diagrams of solution-blended systems.

The most important advantage of physically bonded synthetic macromolecular composites is their processibility at high temperatures, where the network dissociates. Evidently, this feature is their main disadvantage as well. Physically built-up networks have principally short and rigid bridges between the chains. To achieve a sufficient reinforcing effect, the macromolecular compound must contain a high level of physically associable component (i.e., a high concentration of long rigid sequences). Such structures are too rigid and not elastic enough. Thus, although such thermoplastic elastomers have a built-in composite structure with a soft matrix, they must achieve a supplemental composite structure based on blends with softening and tackifying components. They must be formulated (see Chapter 8). From the classic point of view, soft mixing components are low-molecular-weight (low or high modulus) compounds (plasticizers or tackifier resins) that reduce the glass transition temperature (T_g) of the blend and, thus, improve the fluidity of the macromolecular compound.

Advances in sequential block copolymerization allowed the synthesis of (nonassociable) diblocks, which also work like softening, plasticizing components. Thus, both bulky resins (e.g., monomer-based aromatic resins) and nonassociative copolymers (diblocks) can work as diluents of the physically cross-linked network. They cause less cohesion, less elasticity, and less tack. On the other hand, associative or reactive additives (e.g., triblocks, cross-linkers, or tackifiers), which interact with the elastomeric segments of the TPE, can improve the cohesion and elasticity or increase the plasticity (e.g., tackifiers, plasticizers) of the formulation (see also Chapter 8).

The special composite structure of TPEs (see Chapter 3) leads to problems concerning the use of the common adhesive characteristics: shear resistance and tack. Such systems behave as macromolecular composites and display more similarities with filled systems than with elastic networks (see above); the formulation of such systems should differentiate between hardening/elastic reinforcing and softening/tackifying. Principally, for such styrene block copolymers it is possible to improve cohesion with a simultaneous

increase in elasticity (e.g., with triblock or cross-linking agents), to improve cohesion without increased elasticity (with bulky resins or diblocks), to reduce cohesion without increased tack (bulky resins or diblocks), and to reduce cohesion with increased tack (tackifiers, plasticizers). For good cuttability (see Chapter 10 and *Applications of Pressure-Sensitive Products,* Chapter 8) only increased cohesion without increased elasticity is recommended (using bulky resins, diblocks, or micromolecular bulky fillers). On the other hand, for tackifying and processing-related diluting, softening with a simultaneous increase of tack and peel resistance is preferred. SIS block copolymers with high melt flow rates and a relatively high proportion of diblocks were developed. These low-modulus polymers also promote better die-cuttability of PSAs used in label stock applications. Taking into account the different effects of elastic and nonelastic reinforcing additives, the discrepancies between the shear-adhesion failure temperature values and holding power values can be better understood (see also *Fundamentals of Pressure Sensitivity,* Chapter 8, and *Applications of Pressure-Sensitive Products,* Chapter 8). Some years ago, Hamed and Shieh [71] discussed tack as a cohesion-related property. Later, shear resistance was considered as a cohesion- and cuttability-related characteristic [72]. Recent developments in TPEs demonstrate that such generalized assumptions are not valid. The use of shear resistance as an unequivocal index of cohesion or as an index of nonelastic cohesion is incorrect. On the other hand, the use of cohesion as an index of tack is generally not possible. This statement is illustrated by recent advances in the use of the probe tack test method (see also *Fundamentals of Pressure Sensitivity,* Chapter 6).

1.3.2 Pressure-Sensitive Products as Composites on Macromolecular and Macroscopic Scale

According to Ref. [73], polymer-based nanocomposites are attractive materials because of their unique properties resulting from their nanoscale microstructure. Four representative methods exist to produce nanocomposites: exfoliation-adsorption, *in situ* intercalative polymerization, melt intercalation, and template synthesis. Emulsion polymerization is the predominant method used in industry to manufacture a large variety of polymers for various uses such as paint, adhesives, and binders.

Some PSAs, such as chemically cross-linked systems, are composites on a molecular and macroscopic level. In such systems, the site of cross-linking, the concentration of the cross-linking sites, and the flexibility of the cross-linked network are the main parameters that influence the final properties of the adhesive. In the range of chemically cross-linked systems, homogeneous, solvent-based adhesives are relatively simple "constructions," but water-based dispersions possess a very complex build-up. The cross-linking of water-based dispersions is a difficult process because of the high reactivity of water as reaction medium. The reaction of the cross-linking agent with the polymer competes with its reaction with the reaction medium (water). The site of cross-linking (i.e., in the particle or on the particle surface) is yet not clear. Recently, investigations by Frazier et al. [74] demonstrated that the cross-linking reaction of poly(vinyl acetate) copolymers using *N*-methylol acrylamide as curing component occurs on the particle surface.

According to Ref. [75], after being dried the emulsion-based PSA behaves like a filled polymer melt. Although emulsion particles are internally cross-linked to obtain the appropriate viscoelastic behavior, the particles only interact via entangled dangling ends at the interface between particles.

Generally, cross-linking can occur during polymerization or postpolymerization (see Sections 1.1 and 1.2) The polymerization of dienes always leads to partially cross-linked structures. Emulsion polymerization of acrylates carried out to "full" conversion produces significant amounts of microgels inside the particles due to chain transfer to the polymer through hydrogen abstraction [76]. According to Tobing and Klein [77], the main reason for the much lower shear resistance in emulsion-based PSA is discrete microgel morphology, in which the microgels are connected by linear polymer chains by entanglement, in contrast with solvent-borne acrylic cross-linking, as formed after film formation, which resulted in a continuous network morphology. Interlinking of the microgels by covalent bond in the film is needed with the help of a functional monomer (e.g., isobutylmethacrylamide).

In the domain of pressure-sensitive raw materials, styrene–butadiene emulsions are the most important water-based cross-linked systems. A range of various parameters, including the chemical composition (e.g., the styrene content of SBR), the molecular weight, and the sol/gel ratio, describes the adhesive properties of the compound (see also Chapter 2). Because of the corpuscular nature of the particles in water-based systems, gradual cross-linking is possible. Thus, core-shell structures are formed. Spitzer [78–81] investigated the interdependence among polymerization conditions, molecular characteristics, and pressure-sensitive properties of styrene–butadiene latices. For such latices, the balance of the pressure-sensitive properties decisively depends on the glass transition temperature and the molecular characteristics (sol/gel ratio) of the polymer. On the other hand, the maximum peel strength is independent of the gel level and possibly the glass transition temperature [79]. These results indicate that for PSAs in which only the type of the gel differs, the tight gel fraction tends to determine the properties. It is suggested that in such blends the tighter gel is not readily swellable and, hence, poor shear values result. The presence of the "tight" gel promotes adhesive failure as well. In hydrogels (see above) with long-chain cross-linkers (carcass-like cross-linkers) and multifunctional cross-linkers (ladder-like cross-linkers), which lead to tight structures, the same effect of the tight gel on the adhesive properties was reported.

As noted in Ref. [82], a high gel content could compensate for low molecular weight. According to Ref. [76], this was not true for peel behavior.

The strong dependence of pressure-sensitive properties on the rubbery network (gel) characteristics demonstrates that for such polymers the rheologic dynamic mechanical analysis (DMA) data alone do not allow the prediction of pressure-sensitive formulability (see also *Applications of Pressure-Sensitive Products,* Chapter 8). For such copolymers, formulation based on high polymers only (like formulation for acrylics) is also limited.

The composite structure of the adhesive affects its performance as well. Common, solvent-based PSAs, or HMPSAs, do not contain liquid, low-molecular-weight components in their coated and finished status; water-based formulations (dispersions, solutions, or gels) may include an equilibrium level of water due to the technological additives used

(e.g., surfactants, protective colloids, thickeners, solubilizers, fillers, etc.; see Chapter 8) or to the chemical nature of the adhesive. Thus, the adhesive layer possesses a composite structure. The PSA is a composite on a macromolecular as well as a macroscopic scale. The water level in such a construction depends on the environment, time, and temperature and may affect the adhesive properties of the PSA (tack, peel, and especially shear resistance), the converting properties of the adhesive (cutting, slitting, and storage) and the environment resistance (water solubility) of the PSA [36].

Water-based PSAs are composites because of the rest-humidity content of the dried adhesive layer. Although the influence of humidity on the converting properties of PSPs (e.g., guillotine cutting, telescoping by storage, etc.) was evidenced many decades ago [36], progress in this field is lacking. The complexity of such systems as composites increases with mixing. Water-based dispersions can be formulated as blends of various dispersions. For instance, Fabroni and Shull [83] studied the adhesive and mechanical properties of two-component latex films. Several other studies on film formation in blended systems (with particles with different sizes or mechanical properties) have been carried out [84–86].

Adhesive composites containing fillers were investigated as well. Park et al. [73] synthesized and characterized acrylic PSAs reinforced with nanoclay. Such acrylic PSAs were synthesized by emulsion polymerization with a nonionic surfactant in the presence of sodium montmorillonite (Na-MMT). This indicates that the tack and peel strength of PSAs demonstrate their maximum values at 1% bw of Na-MMT content. Li et al. [87] reported that ball tack values decreased when the montmorillonite was loaded in the PSA matrix, because the MMT loading increased both the storage modulus and the T_g of PSAs. Patel et al. [88] prepared nanocomposite adhesives based on acrylics and silica or clay. They observed significant peel strength improvement with nanofiller concentration (1–6% bw) and the locus of failure changed from interfacial failure to stick–slip failure for the composites.

Generally, the "composite degree" of PSAs depends on their physical status. As discussed in Ref. [89], the concentration of the adhesive components in the formulated PSA composition decreases as follows.

$$\text{HMPSA} > \text{solvent-based PSA} > \text{water-based PSA} \tag{1.3}$$

Table 1.7 presents the composite structure of PSPs on a molecular and macroscopic scale. Intramolecular heterogeneity is caused by sequence length, build-up and distribution, molecular weight distribution, and cross-linking, as well as by intramolecular segregation due to cross-linking, crystallization, filler effect, and segregation. Both, intramolecular and intermolecular composite structures affect the adhesive, converting, and end-use performance. The composite structure on a macroscopic scale, characterized by visible phase separation and due to disperse or filled systems, is illustrated. Table 1.8 presents the composite structure of PSPs as a laminated, that is, finished product.

1.3.3 Pressure-Sensitive Products as Composites on a Laminate Scale

When two materials with different characteristics on a macroscopic level are joined to obtain a multimaterial or composite system, the properties of the composite are a

TABLE 1.7 Composite Structure of PSPs on a Molecular and Macroscopic Scale

Parameters of Heterogeneity, Intramolecular	Source of Heterogeneity	Composite Structure Effects
Composite on a Molecular Scale		
Sequence length, build-up, and distribution	Reactivity ratios, polymerization mechanism	Intermolecular interactions, reactivity, T_g, modulus, fibrillation, processing of PSA, adhesive properties
Molecular weight distribution	Polymerization mechanism	Reactivity, compatibility, intermolecular reactions, fibrillation, processing of PSA, adhesive properties
Cross-linking	Monomer reactivity	Reactivity, intermolecular reactions, processing of PSA, adhesive properties
Parameters of Heterogeneity, Intermolecular		
Cross-linking	Reactive functional groups, associative functional groups, or sequences, sequence build-up and length, reactive fillers	T_g, modulus, compatibility, thermal stability, tack, peel, and shear resistance, removability, dissolution, processing, cutting ability
Crystallization	Monomer build-up, polymer build-up, long-side-chain processing conditions	Modulus, compatibility, thermal stability, tack, peel, and shear resistance, removability, dissolution, processing, cutting ability
Filler effect	Sequence build-up, incompatible polymers, incompatible tackifiers, fillers	T_g, modulus, compatibility, thermal stability, tack, peel, and shear resistance, removability, processing, curing, drying, cutting ability
Phase separation	Incompatibility or partial compatibility	Dependence of adhesion properties on tackifier level, topography
Composite on a Macroscopic Scale		
Visible phase separation		
Disperse system	Polymerization technology, recipe	Site of polymer analogous reactions; polymer structure, time/temperature stability of adhesive, rheology of liquid adhesive, shear stability of liquid adhesive, coatability, drying, composite structure of dry adhesive; tack , peel, and shear resistance, removability, water-resistance
Filled system	Chemical and physical additives, incorporated air and humidity, insufficient drying, migration from carrier and liner	Time/temperature stability of adhesive, rheology of liquid adhesive, shear stability of liquid adhesive, coatability, drying, composite structure of dry adhesive; tack , peel, and shear resistance, removability, water-resistance, migration, lay-flat, shrinkage, printability, converting and application properties, laminate build-up

TABLE 1.8 Composite Structure of PSPs on a Laminate Scale

Composite on a Laminate Scale		
Laminate Components as Composite	Source	Effects
Carrier material	Material, processing technology, geometry, pre- and postprocessing, mono- or multiple construction, stress/strain and chemical history	Choice of PSA, coating method, drying, coating weight, composite structure of PSA, time/temperature stability of PSA, mutual interactions, anchorage, coating weight, coating weight tolerances, tack, peel, and shear resistance, removability, choice of liner, converting properties, application, build-up of the laminate
PSA	Physical state of adhesive, additive's type and level, coating image, drying curing of adhesive, geometry of PSA, interactions with other laminate components	Choice of carrier material, geometry of carrier, coating method, coating weight, coating image, precoating, pretreatment of carrier, post coating, tack, peel, and shear resistance, removability, water resistance, converting properties, shrinkage, lay-flat, migration, laminate build-up
Liner	Carrier material for liner, geometry, release material for liner, coating method, interactions with adhesive	Choice of PSA, coating method, drying, coating weight, composite structure of PSA, time/temperature stability of PSA, mutual interactions, tack, peel, converting and application properties, build-up of the laminate
PSP Laminate Construction as Composite	Source	Effects
Monoweb	Material, pre- and posttreatment, post- and precoating, lamination conditions	PSA choice, anchorage, adhesive and converting properties
Multiweb	Carrier and PSA choice, coating methods, lamination conditions, storage, die-cutting	Adhesive and converting properties, end-use application methods

function of the properties of the two basic materials but also, and essentially, of the interaction force between those materials developed in a spatial region along the interface. In reality, no bonding is 100% perfect. Achenbach and Zhu [90] introduced the concept of imperfect interface defined by the interface parameters. Van Dijck et al. [91] developed a simple method for a first approximation of the interaction level between layers in a laminate or an adhesively bonded joint.

PSPs are composites on a laminate scale also. For instance, a label may have a laminated carrier (composite 1) that is coated with an adhesive (composite 2), which is laminated together with a liner (composite 3) to build up the label (composite 4). For this composite, the geometry of the carrier as well as that of the PSA are determinant.

In *Applications of Pressure-Sensitive Products,* Chapter 3, Chang and Holguin describe a special, *in situ* made pressure-sensitive composite based on a curable label construction comprising a curable PSA layer (1–2 μm thick) and curable epoxy layer (0.5–1.5 μm thick) coated onto a transparent carrier film.

The viscoelastic properties of the adhesive (Φ_a) depend on the viscoelastic properties of the bulk adhesive (Φ_{ab}) and on those of the composite adhesive layer (Φ_{ac}), or

$$\Phi_a = f(\Phi_{ab}, \Phi_{ac}) \tag{1.4}$$

The viscoelastic properties of the bulk adhesive are different from those of the composite material. Generally, the viscoelastic properties of composite solvent-based adhesives are superior to those of the bulk material. The viscoelastic properties of water-based (composite) PSAs are inferior to those of the bulk adhesive. This behavior can be explained by the different nature of the formulation additives (see also Chapter 8).

The influence of the composite structure of the pressure-sensitive laminate on its converting properties was discussed in detail by Benedek in Ref. [92]. The composite structure of the adhesive and the laminate construction of the PSP both affect the stiffness and the cuttability of the PSP. The main components of PSPs are multilayer structures. Their properties are determined by the nature, number, geometry, and mutual interaction of such layers. The classic PSPs are carrier based, where the carrier ensures the mechanical properties of the laminate and the adhesive provides the pressure sensitivity (see *Applications of Pressure-Sensitive Products,* Chapter 1). *Ad absurdum,* the carrier is nondeformable, and the adhesive must be deformable. The development of nonpaper carrier materials provided webs that do not fulfills this statement; they possess deformability and self-adhesivity. Thus, the role of the carrier as a nondeformable, nonadhesive component is not valid.

The modulus of adhesive joints depends on the adhesive's thickness [93]. In fact, increasing the thickness of the adhesive layer decreases its modulus. This behavior may be explained by the special, multilayer structure of the adhesive and the influence of the surface of the solid-state components. The modulus of the laminate varies close to the interface with the adhesive. The width of this zone depends on the adhesive; for certain adhesives it varies between 0.04 and 0.2 mm [94] (see also *Fundamentals of Pressure Sensitivity,* Chapter 4). However, the thickness (coating weight) of the adhesive would also exert a special influence on the adhesive resistance for PSA laminates. Increasing the coating weight increases the thickness of the mobile middle adhesive layer only (i.e., the cold flow of the adhesive). According to the paradox of Griffith [95], a fiber-like material possesses a much higher strength than the same material in another form. The paradox of tensioning or stressed length influences the effect of the thickness of the adhesive and of the primer as well. The change of the modulus of the constrained PSA in a sandwich structure was taken into account by Kauzlarich and Williams [96]. Another parameter influencing the modulus of plastics is their degree of orientation [4]. No data are available regarding a similar modulus dependence for PSAs.

One should note the dependence of the modulus on the composite structure of the laminate or laminate components. Special attention must be paid to the influence of the humidity on the paper modulus (which may depend on the humidity of the water-based adhesive layer; see above).

For a classic PSP based on a solid-state carrier material and a fluid adhesive, the properties of both components depend on their mechanical characteristics and geometry. The chemical nature, macromolecular characteristics, processing technology, and build-up of the carrier, together with its thickness (geometry), influence its conformability during bonding and its deformability during debonding. The deformability of the carrier during debonding affects the debonding angle, the transfer of the debonding energy, and the thickness of the adhesive (see also *Applications of Pressure-Sensitive Products,* Chapter 8). Such parameters are determinant for removability. The use of carrier deformability as an instrument to regulate adhesive characteristics was discussed in detail in Ref. [82]. As discussed in Refs [33,36], the laminate construction (build-up, components, and number of components) affects the peel resistance as well.

The thickness of the adhesive expressed as the coating weight (C_w) influences its conformability and stress transfer, that is, the bonding and debonding characteristics (tack, peel resistance, and shear resistance) [4,97,98]. The role of coating weight has been studied by several authors [82,99–102] (see also *Applications of Pressure-Sensitive Products,* Chapter 8).

According to Ref. [102], the effect of the adhesive thickness on the bond strength of adhesive joints is still not perfectly understood. Classic analyses predict that the strength increases with adhesive thickness, whereas experimental results demonstrate the opposite. Various theories have been proposed to explain this discrepancy, such as the theory of Crocombe [103] in 1989, based on the plasticity of the adhesive, but there is a lack of experimental evidence. Crocombe [103] demonstrated that thicker joints have a lower strength with the plasticity of the adhesive. Another theory to explain the effect of the adhesive thickness on the single lap joint strength was introduced by Gleich et al. [104]. The interface stresses that increase with adhesive thickness could therefore justify the fact that thicker joints are weaker. Another earlier theory proposed by Adams and Peppiatt [105] explains the discrepancy by noting that thicker bondlines contain more defects, such as voids and microcracks.

To avoid its influence on the properties of commercial PSPs, the coating weight values are normed (see *Applications of Pressure-Sensitive Products,* Chapter 8); that is, the coating weight values used in practice are situated in a domain where the dependence of the adhesive properties on the coating weight is minimal and the coating weight tolerances are well defined. The best known correlations concerning the influence of the coating weight on the adhesive properties are determined in such standardized domains.

In practice, the dependence of the peel resistance on the coating weight is complex, and the plot (an *S*-shape curve) presenting this dependence includes different domains as a function of the adherend surface, carrier material, and adhesive characteristics [36,106] (see also *Applications of Pressure-Sensitive Products,* Chapter 8). At low, subcritical coating weight values there is no sufficient adhesion; at upper critical coating weight, increased coating weight causes increased peel resistance (term C_w^{α} in the mathematical correlation between peel resistance and coating weight), and over a certain coating weight value, peel resistance does not depend on the coating weight. In practice, according to the (simplified) correlation (Equation 1.5), a reduction in coating weight decreases peel resistance, and at extremes it can lead to a subcritical thickness of the adhesive layer, which does not provide sufficient adhesion. Thus, the dependence of the

peel resistance (P) on the coating weight (C_w) is not monotonous, but obeys different mathematical laws in various coating weight domains, where changes in bond force as well as bond failure are controlled by the coating weight,

$$P = f(C_w^{\alpha} - k_1) \tag{1.5}$$

where k_1 is a constant that describes the critical coating weight (C_{wcr}). In a similar manner, the dependence of peel resistance on the carrier thickness can be described by the following (simplified) correlation,

$$P = f[(F_m^{\gamma} - k_2)] \tag{1.6}$$

where F_m is the maximum tensile strength of the (plastic film) carrier material, and the coefficient k_2 takes into account the minimum film thickness required for dimensional stability of the carrier. In the whole domain of variables, the correlation among adhesive thickness, carrier strength, and peel resistance can be written as follows.

$$\mathrm{P} = f[(C_w^{\alpha} - k_1), (\mathrm{F}_m^{\gamma} - k_2)] \tag{1.7}$$

That means that there is also a critical carrier deformability (i.e., critical carrier strength F_{mcr}). The critical coating thickness (coating weight) value and critical carrier thickness (carrier strength) value together determine the practical usability of a pressure-sensitive laminate. These parameters are correlated.

$$C_{wcr} = f(F_{mcr}) \tag{1.8}$$

Subcritical carrier strength due to subcritical carrier thickness leads to excessive carrier elongation and, thus, causes decreased coating weight. In this manner, the coating weight may also attain its critical value; that is, joint failure occurs.

As a consequence, nondestructive deformation (no break but excessive elongation) of the carrier material (strain) can also lead to a destructive modification of the adhesive joint due to the change in adhesive thickness. As noted by Benedek [36], for monoextrudates with a film thickness of about 35 μm, the critical values, F_m, are of 8–9 N; for coextrudates such values are reached at a lower thickness, about 20 μm.

In the above case, in practice, joint failure occurs during delamination. Under static conditions of storage, where no deformation of the carrier material occurs, such PSA (protection) films may work satisfactorily; that is, they adhere to the surface to be protected with the nominal value of adhesion. On the other hand, tests of peel resistance (dynamic use of the joint) can lead to excessive carrier deformation, which means for thin deformable pressure-sensitive laminates there is a difference between their usability and their debonding ability, or testing behavior. Such thin protective films cannot be tested using common test methods (see also *Applications of Pressure-Sensitive Products,* Chapter 8). In this case, there is a difference between the static and dynamic criterion of usability.

Further investigations are required to optimize the critical carrier thickness as a function of the carrier material and its construction, to optimize the critical carrier

thickness as a function of the adhesive, to mathematicize the correlation between the mechanical strength of the carrier material and peel resistance, to measure the adhesive and carrier deformation during joint failure caused by carrier deformation, and to elaborate upon an adequate test method for the static test of thin, deformable protective films. For manufacturers the mutual influence of adhesive and carrier thickness limits downgauging of the carrier film or imposes a higher coating weight.

This problem is even more complex because in industrial practice for such thin PSP constructions (most removable protection films), a primered adhesive is used. The adhesive itself is a multilayer construction (see also *Applications of Pressure-Sensitive Products,* Chapter 1) and, as described by Benedek in Ref. [64], primered constructions use less coating weight. Recently, Carelli et al. [107] examined the adhesive properties of bilayer constructions to optimize the adhesive properties. Because the resistance to crack propagation is mainly an interfacial property, whereas shear resistance is mainly a bulk property of the PSA, they explored the possibility of working with bilayer PSAs, where an interface layer would be softer and more dissipative and the other would be more rigid and less dissipative. "Translated" into industrial language, this is the common use of primers. For instance, isocyanate cross-linked rubber–resin-based PSAs for protection films use the same adhesive as primer, with more cross-linking agent, that is, a more rigid and less dissipative layer. Carelli at al. confirmed the old industrial experience that adhesive properties can be significantly modified using bilayer systems, and the use of a gradient in composition is an option to improve adhesion. Moreover, it offers the possibility of improving removability. In a similar manner, the "old" statement of Benedek [97] concerning the decisive role of the configuration (order of the layers, soft/rigid) was confirmed as well. Industrial practice generally uses a rigid primer combined with a soft adhesive.

Summa summarum, PSPs must be discussed as composites on a macromolecular, formulation, and construction level, where the build-up of the components decisively influences the final properties of the product. On a macromolecular and formulation scale, the build-up of network structures (physical or chemical) makes the use of common rheologic notions and DMA questionable. On a manufacturing level, the rheology, mechanical characteristics, and geometry of the adhesive and of the carrier material limit the use of standard test methods and impose the design of PSPs as a construction.

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2

Rubber-Based Pressure-Sensitive Adhesives

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Natural rubber (NR) was the first base polymer for early pressure-sensitive adhesives (PSAs) intended for medical plasters (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Later, the use, formulation, and application of rubber-based PSAs was widely studied and sophisticated materials have been obtained. Today, the rubber-based PSA can be considered an innovative material because industrial and academic interest is under continuing development.

Rubber-based adhesives are probably the most commonly known family of adhesives on the general market. The development of these adhesives from natural sources and the possibility of modifying their properties by incorporating synthetic materials make them one of the most interesting materials for adhesives formulators. Furthermore, the broad range of applications and performance (from structural to temporary joints), the broad range of modifications in properties determined by the tackifier–rubber compatibility, and the choice or not of vulcanization renders the understanding of rubber-based PSAs fascinating.

Although rubber-based PSAs have been widely used for the past 100 years, only a few excellent books contain information about them. Some of the most significant contributions in this area are listed under Refs [1–7].

Several chapters in the above-mentioned books contain interesting and detailed information about specific rubber-based PSAs. There is no reason to produce another comprehensive compilation of data of the main rubber-based PSA families, so the author prefers to provide a more general overview of the main features of these adhesives, paying special attention to the components used to formulate the adhesives and to the main distinct properties that can be achieved by incorporating several ingredients in manufacturing. Although many practical aspects related to the technological aspects of rubber-based adhesives are discussed in this chapter, an effort was made to include more fundamental issues related to adhesion (see also *Fundamentals of Pressure Sensitivity*) and the influence of the elastomer–resin compatibility on different properties of these adhesives (see also Chapters 3 and 8). Further, special attention was paid to the manufacture, chemistry, and characterization of the main ingredients in rubber-based PSA formulations, because the information is widely distributed.

The specific formulations and manufacturing procedures of rubber-based adhesives have not been considered in this chapter. These features are discussed in Chapters 8 and 10. Furthermore, adhesives based on block copolymers [styrene–butadiene–styrene, styrene–isoprene–styrene, etc.] were not included in this chapter. This class of adhesives is described by Hu and Paul in Chapter 3. Readers interested in these aspects can find detailed information in *Handbook of Adhesives*, 3rd ed. (Van Nostrand Reinhold, New York, 1990), *Pressure-Sensitive Adhesive Formulation* (VSP, Utrecht, The Netherlands, 2000), and *Adhesion Science and Engineering—2. Surfaces, Chemistry and Applications* (Elsevier, Amsterdam, 2002). Finally, one must keep in mind that the ingredients and performance of rubber-based PSAs and common rubber-based adhesives are relatively similar.

This chapter includes the following aspects.

1. General characteristics of rubber-based adhesives.
2. Main features of rubber-based adhesives.
3. Structure, chemistry, and properties of the main ingredients in rubber-based PSAs (the rubber and the resin in more detail).
4. The main general characteristics and properties of rubber-based adhesives, including some specific applications. Specific updated aspects related to formulation, ingredients, and adhesion are also provided.

2.1 Introduction

Rubber-based adhesives, also called elastomeric adhesives, are widely used in industrial and household applications. In fact, about one-third of the adhesives used in the world are made from natural or synthetic rubbers. Some of the elastomeric adhesive systems demonstrating industrial importance in recent years are pressure-sensitive tapes and labels, construction adhesives, contact adhesives, hot-melt packaging and bookbinding adhesives, and high-strength structural applications for aircraft, automotive, and construction.

Some rubber-based adhesives need vulcanization to produce adequate ultimate strength and the adhesion is mainly due to chemical interactions at the interface. Other

rubber-based adhesives (contact adhesives) do not necessarily need vulcanization, but require adequate compounding to produce the adhesive joints, mainly with porous substrates. In this case, the mechanism of diffusion dominates their adhesion properties. Consequently, the properties of the elastomeric adhesives depend on both the variety of intrinsic properties in natural and synthetic elastomers and the modifying additives that may be incorporated into the adhesive formulation (tackifiers, reinforcing resins, fillers, plasticizers, curing agents, etc.).

2.1.1 Brief History of Rubber-Based Adhesives

The first elastomeric adhesive was prepared by the end of the 18th century and consisted of naphtha solutions of NR. This kind of adhesive is still in use for the production of temporary joints in textiles, art material, and footwear (where there are specifically labeled cement adhesives). One of the early applications of NR-based adhesives was the lamination of textile products to impart waterproof resistance. For this application cross-linking (vulcanization) of the adhesive after application was necessary. Adhesives made with NR latex were first prepared in the middle of the 19th century. Organic solvents were used to manufacture these adhesives, which generally contain rosins (a natural product derived from pine sap). However, the strength provided by these formulations was poor and, in general, porous substrates (e.g., paper, leather, textiles) were necessary to produce acceptable joints.

During World War II several new synthetic elastomers were produced and new types of adhesives (mainly styrene–butadiene and acrylonitrile copolymers) were manufactured to produce adequate performance in joints produced with new difficult-to-bond substrates. Furthermore, formulations to work under extreme environmental conditions (high temperature, resistance to chemicals, and improved resistance to aging) were obtained using polychloroprene (Neoprene) adhesives. Most of these adhesives require vulcanization to perform properly.

Structural applications of rubber-based adhesives were also obtained using rubber-thermosetting resin blends, which provided high strength and low creep. The most common formulations contain phenolic resins and polychloroprene or nitrile rubber and always need vulcanization.

Thermoplastic block copolymers were used for rubber-based PSA and rubber-based hot-melt adhesives from the mid 1960s. These adhesives found applications in packaging, disposable diapers, labels, and tapes, among other industrial markets. The formulation of such adhesives generally includes an elastomer (principally containing styrene endblocks and either isoprene, butadiene, or ethylene–butylene midblocks) and a tackifier (mainly a rosin derivative or hydrocarbon resin), see also Chapters 3 and 8.

2.2 Contact Adhesives

One of the most common classes of rubber-based adhesives is the contact adhesives. In a broad sense, contact adhesives can be considered PSAs, because tackiness is a key property and pressure must be applied for joining (see also *Applications of Pressure-Sensitive Products*, Chapter 1). These adhesives are bonded to themselves by a diffusion

process in which the adhesive is applied to both surfaces to be joined. To achieve optimum diffusion of the polymer chains, two requirements are necessary: (i) high wettability of the adhesive by the smooth or rough substrate surfaces and (ii) adequate viscosity (in general rheologic properties) of the adhesive to penetrate into the voids and roughness of the substrate surfaces. Both requirements can be easily achieved in liquid adhesives (for the role of the diffusion in adhesion, see Chapter 3 and *Fundamentals of Pressure-Sensitivity*, Chapter 2.). Once the adhesive solution is applied on the surface of the substrate, spontaneous or forced evaporation of the solvent or water must be produced to obtain a dry adhesive film. In most cases, the dry contact adhesive film (a PSA!) contains residual solvent (about 5–10 wt%), which usually acts as a plasticizer.

Environmental conditions under which solvent release from the adhesive on the substrate is produced must be carefully controlled. Humidity is critical because loss of heat due to solvent evaporation may allow the dew point to be reached (evaporation of the solvent is an endothermic process), and then condensation of water on the adhesive can be produced. This phenomenon is often called *moisture blooming*. The presence of water on the adhesive film causes a detrimental effect because the autoadhesion of rubber chains is greatly inhibited. Therefore, humidity must be controlled and avoided by increasing the temperature during solvent evaporation.

The dry adhesive films on the two substrates to be joined must be placed in contact to develop adequate autoadhesion. For example, diffusion of polymer rubber chains must be achieved across the interface between the two films to produce intimate adhesion at the molecular level. The application of pressure or temperature for a given time allows the desired level of intimate contact (coalescence) between the two adhesive film surfaces. The rheologic and mechanical properties of rubber-based adhesives will determine the degree of intimacy at the interface. Those properties can be optimized by selecting the adequate rubber grade, the nature and amount of tackifier, and the amount of filler, among other factors.

The diffusion process in natural and polychloroprene rubber adhesives can be explained using Campion's approach [8], which considers the concept of molecular free volume. This free volume is mainly affected by the solvent mixture of the adhesive (which will determine the degree of uncoiling of rubber chains) and by the ingredients in the formulation (mainly the amount and type of tackifier).

2.3 Specific Features of Rubber-Based PSAs

The chemical nature and molecular weight of the rubber will greatly determine the properties of the PSAs. However, some common characteristics can be found in most rubber-based PSAs, as follows.

1. *Broad range of substrates for assembly*. Rubber PSAs can be used to joint several substrates in a temporary or permanent way. Although for many applications curing (i.e., cross-linking or vulcanization) is not necessary, to provide high strength and (mainly) heat and chemical resistance, vulcanization is mandatory. Removability (e.g., for protection films) requires cross-linking as well (see *Applications of Pressure-Sensitive Products*, Chapter 4).

2. *Flexibility.* The resilience of rubber helps to absorb the stresses applied to the joints. Therefore, these adhesives properly resist impact, shear, elongation, vibration, and peel stresses.
3. *High peel strength.* The intrinsic properties of rubbers (high ability to produce high elongation under stress) impart adequate strength to the joints under peeling forces. However, rubber-like polymers demonstrate poor resistance to shear stresses.
4. *Versatility of formulation.* Several types of elastomers can be used in elastomeric adhesives. For each family of rubber, several grades and different chemical modifications (e.g., grafting of polymers) can be achieved to impart specific properties to the joints. Furthermore, specific rubber-based PSA formulations for particular end uses can be easily achieved by adding several ingredients (fillers, reinforcing agents, etc). However, the basic properties of the formulations are provided by the rubber nature.
5. *High green strength.* This is one of the most important properties of rubber-based PSAs. The *green* (immediate) *strength* can be defined as the ability to hold two surfaces together upon first contact and before the adhesive develops its ultimate bonding properties when fully cured. In other words, the green strength is the intrinsic capacity of adhesives to strongly adhere to the substrates immediately after application. The green strength can be modified by changing the solvent composition (for solvent-borne adhesives) or by incorporating ingredients into the formulations (mainly tackifiers). Green strength is essential in pressure-sensitive rubber-based adhesives (PSA) and in some polychloroprene rubber–phenolic resin blends.

Rubber-based adhesives develop strength faster than most other polymeric types. Figure 2.1 [9] illustrates the differences in the development of peel resistance for several rubber polymers (without additional additives, except an antioxidant). NR and styrene–butadiene rubber provide higher initial peel resistance values. As time after joint formation progresses, polychloroprene and nitrile rubber develop much higher peel resistance, particularly after a few hours.

2.4 Ingredients of Rubber-Based PSAs

Rubber-based PSAs typically contain an elastomer and a tackifying or modifying resin as the key components, but other ingredients are also included (see also Chapters 3 and 8). The formulation of rubber-based PSAs may contain up to eight different components, such as elastomers, resins, plasticizers or softeners, fillers, curing agents, antioxidants, solvents, and other additives (e.g., pigments, biocides, etc.; for formulation additives see also Chapter 8). In general, most rubber-based PSAs do not contain all the previous ingredients. As typical examples, the composition of two rubber-based PSAs is given in Tables 2.1a and 2.1b.

The amounts of the different ingredients are only orientative. The composition of rubber-based adhesives can be expressed as a percentage, a weight percentage, or, more

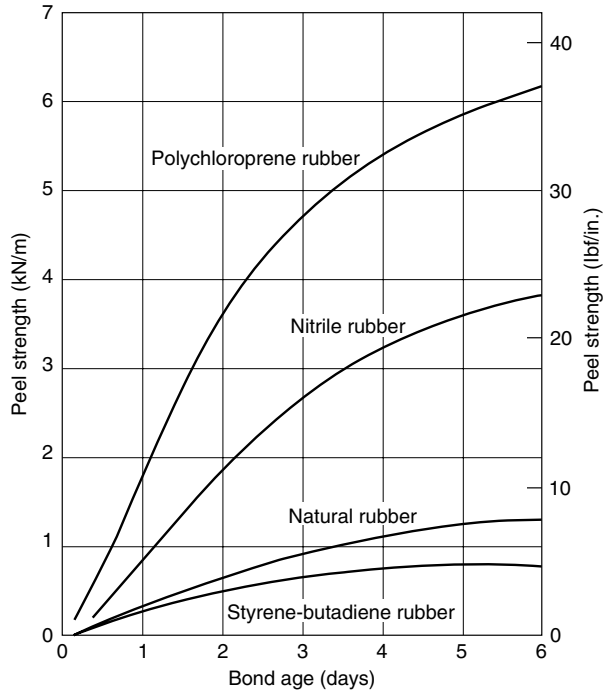


FIGURE 2.1 Bond strength development at room temperature as a function of time for different rubbers (From Coe, D.G., *Neoprene Solvent Based Adhesives*, Technical Bulletin ADH-100.1 (R1), E.I. Du Pont de Nemours. With permission.)

TABLE 2.1a Typical Formulation of Rubber-Based PSA for Surgical Tape

Ingredient	Percentage (phr)
Elastomer	100
Tackifier	150
Lanolin	25
Zinc oxide	50
Antioxidant	1
Solvent mixture	400

TABLE 2.1b Typical Formulation of Rubber-Based PSA for Carpet Tiles

Ingredient	Percentage (phr)
Elastomer 1	75
Elastomer 2	25
Hydrocarbon resin tackifier	100
Plasticizer	50
Calcium carbonate	100
Antioxidant	5

commonly, as parts of one component with respect to 100 parts elastomer (phr). In this chapter compositions in phr will generally be used.

Some general aspects are related to the formulation of rubber-based PSAs. Resins can be added to improve tack, wetting properties, heat resistance, bond strength, and oxidation resistance. The most common resins used in rubber-based PSAs are rosins, rosin esters, terpene, coumarone–indene, hydrocarbon, and phenolic resins (see also Chapter 8). Plasticizers and softeners reduce hardness, enhance tack, and decrease the cost of rubber adhesive formulations. Paraffinic oils, phthalate esters, and polybutenes are typical plasticizers (see also Chapter 8). Fillers are not commonly added to rubber-based adhesive formulations because they reduce adhesion, but decrease cost and help to control rheology (see also Chapter 8). Clays, calcium carbonate, and silicates are the most common fillers in rubber-based PSA formulations.

In the following sections, the manufacture, chemistry, and properties of the main ingredients of rubber-based PSAs will be considered.

2.4.1 Elastomer

Rubber is composed of very large molecules containing thousands of atoms, arranged one after another in a string-like manner. The arrangement of the atoms repeats in a regular cycle, so the structure can be considered as a certain segment that is repeated *n* times. The polymerization of the monomers with one double carbon–carbon bond proceeds by opening up to form links between the repeating segments. As the molecular weight increases, the density, melting point, and boiling point increase, with the last property increasing to the point where the material decomposes before it evaporates. High molecular weight is necessary for strong, load-bearing rubbers. Viscosity is roughly proportional to the molecular weight of the rubbers.

The least complicated repeating unit in a polymer corresponds to ethylene. The regular repeating structure of polyethylene (PE) allows neighboring segments to align in perfect order to form crystals. To make a rubbery polymer, it is necessary to minimize crystallization by breaking up the structural regularity of the repeating $-CH_2-$ segments. There are two ways to prevent regular alignment in rubbers.

1. Add side groups such as methyl or chlorine. The methyl group (for instance in ethylene–propylene rubber) prevents neighboring chain segments from aligning perfectly.
2. Include unsaturation or double carbon–carbon bonds in the polymer chain. Diene monomers have two double carbon–carbon bonds and polymerize in such a way that the repeating segments are joined at the extreme carbon atoms with the other double bond remaining in each segment. These remaining double carbon–carbon bonds prevent rotation, hindering the alignment of the molecular segments and disturbing crystallization. Styrene–butadiene rubbers are noncrystallizing polymers containing unsaturation (see also Chapter 3).

Both side groups and double carbon–carbon bonds can be incorporated into the polymer structure to produce highly resilient rubbers. One typical example is polyisoprene (PI) rubber.

TABLE 2.2 Some Properties of Elastomers Used in Rubber-Based PSAs

Elastomer	Density (g/cm^3)	T_g (°C)	Max. Service T (°C)
Natural rubber	0.91	−75	70
Butyl rubber	0.92	−65	100
Styrene–butadiene rubber	0.93	−55	70

When temperature is lowered, rubbers become stiff and brittle. All rubbers eventually stiffen to a rigid, amorphous glass at the glass transition temperature (T_g). This temperature also indicates the low-temperature service limit of the rubber. T_g values are dependent on the structure, degree of cross-linking (vulcanization), and isomer composition of the rubber (see also Chapter 3).

The physical properties of rubbers are mainly determined by the molecular weight and the structure of the repeating units. By making branched chains rather than linear ones, low-viscosity polymers for solution applications are obtained. By lightly cross-linking to form an insoluble or gel polymer, better extruding polymers can be obtained. By broadening the molecular weight distribution, polymers that mix more easily can be obtained.

Several elastomers can be used in rubber-based PSAs, mainly NR, butyl rubber (BR), polyisobutylenes (PIB), and styrene–butadiene rubber. Typical properties of these rubbers are given in Table 2.2. The elastomer provided the backbone of the adhesive, so the main performance of the adhesive is provide by the rubber properties. However, several specific properties for application are imparted by adding other ingredients to the formulations.

2.4.1.1 Natural Rubber

NR can be obtained from the sap of a number of plants and trees. The most common source is the *Hevea brasiliensis* tree. Although NR was known in Central and South America before the arrival of Christopher Columbus in 1492, its first use as an adhesive was established in a patent dated 1891. As rubber became an important part of the industrial revolution, the rubber adhesives market grew in importance. To comply with the increasing demand for NR materials, plantations of *H. brasiliensis* trees were established in Southeast Asia in the early 20th century, mainly to meet the demand of the automobile industry.

NR is harvested as latex by tapping trees in a similar manner as for maple syrup. Tree latex contains about 35 wt% rubber solids, as well as small quantities of carbohydrates, resins, mineral salts, and fatty acids. Ammonia should be immediately added to the latex to avoid coagulation by these other ingredients and to prevent bacterial degradation. After collection, the latex can be concentrated to 60–70% solids if the latex product is required for end use. Otherwise, the latex is coagulated, washed, dried, and pressed into bales for use as dry rubber.

NR latex grades are described by the method of concentration used. Evaporation, creaming, and centrifuging are the most common methods used in the industry.

1. *Evaporated latex* is produced by heating at a reduced pressure, and the ammonia is replaced by potassium hydroxide containing a small amount of soap to assist

with stabilization. It has a solid content of about 73%. This NR latex grade demonstrates improved resistance to aging and is adequate when a high level of fillers must be added during formulation.

2. *Creamed latex* is obtained by adding fatty acid soap and a creaming agent (e.g., an alginate) in a tank; separation of the creamed layer from the serum must be completed. The solids content in the creamed rubber is 66–69%. This grade of NR is not interesting to adhesive manufacturers.
3. *Centrifuged latex* is the most important and common type of NR (about 95% of latex production). Water-soluble nonrubber components are removed by centrifugation. Solids content ranges from 50 to 67%. This NR latex grade is preserved by adding 0.7% ammonia.

In solid form, NR is graded according to the content of dirt remaining from the precipitation of latex at the plantation. Eight basic NR types have been traditionally recognized internationally. Only the so-called *ribbed smoked sheets* and *pale crepes* are normally used for adhesives. However, the predominant grade system used since 1965 is the Standard Malaysian Rubber system.

Some aspects of the raw dry NR grades for adhesive manufacturing must be considered. NR tends to suffer oxidative degradation catalyzed by metals (mainly copper). The susceptibility of NR to oxidation can be measured using the plasticity retention index. Better grades of rubber have a higher plasticity retention index.

On the other hand, during storage an increase in the viscosity and gel content of NR latex can be produced (*storage hardening*). The presence of aldehyde groups on the rubber chain may produce cross-linking reactions, which are responsible for the formation of gel. The addition of small amounts of hydroxylamine to the latex before coagulation helps to prevent storage hardening.

To avoid agglomeration of dry rubber particles during storage and manipulation, an antitack agent (calcium stearate, for example) is commonly added. The chemical composition of NR mainly corresponds to *cis*-1,4-PI (Figure 2.2).

Natural latex is polydisperse (the size of individual particles may vary from 0.01 to 5 μm). Synthetic latex has a relatively narrow particle size, and therefore the viscosity at a given rubber content is higher in synthetic rubber (PI) solutions. The average molecular weight is typically about 1 million g/mol and depends on the gel content.

The main characteristics of NR latex are high gel content, high molecular weight, high cohesive strength, high self-adhesion and high solids content. Chemically modified NR grades are available on the market. The most common grade is a methyl methacrylate (MMA) graft polymer called *Heveaplus MG*, in which the NR backbone contains polymethyl methacrylate side chains. Heveaplus latex contains about 50% solids. Although there is always some MMA homopolymer in the latex, at least 50% is grafted.

Depolymerized liquid NR is prepared by extensive mastication of NR in air at 250°C in the presence of a peptizing agent. Depending on the time

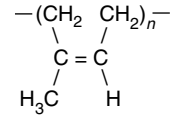


FIGURE 2.2 Chemical structure of the cis-1,4-polyisoprene.

of treatment, several viscosities can be obtained. This material is soluble in many organic solvents but not in alcohols or ketones and is compatible with many drying oils and ester-type plasticizers. Chemically depolymerized latex exhibits good peel resistance without the addition of resin [10], and because the glass transition temperature of NR is not affected by the reaction, these materials can be used in low-temperature applications.

The increasing demand on NR for several applications and the increased production cost (labor, transportation, relatively low added value of NR in the market) allows the manufacture of synthetic PI as an alternative to NR. Although PI should replace NR in adhesive formulations, there are some differences in molecular weight and gel content and in the content in the *trans* isomer. Therefore, the gel-free nature of PI gives solubility in organic solvents without mastication, but relatively poorer tack and green strength are obtained compared with NR. With respect to the vulcanizing adhesives, formulations containing PI tend to cure more slowly and need the addition of higher amounts of tackifier than in NR formulations.

2.4.1.2 Butyl Rubber and Polyisobutylenes

BR and PIB are widely used in adhesives (see also Chapter 4) and self-adhesive films (see *Applications of Pressure-Sensitive Products*, Chapter 7) as primary elastomeric binders and as tackifiers and modifiers. The main difference between these polymers is that BR is a copolymer of isobutylene with a small amount of isoprene (which introduces unsaturation due to carbon–carbon double bonds), whereas PIB is a homopolymer.

The chemical structure of BR (Figure 2.3) is mainly composed of a long and straight carbon–hydrogen backbone, containing between 47,000 and 60,000 units (see also Chapter 4). The small percentage of isobutene provides some degree of unsaturation (generally lower than 2% of that found in NR) to allow curing, but at the same time renders BR very stable and inert to weathering, aging, and heating. BR has a good resistance to oils and chemicals and has very low water absorption [11]. The many side groups attached to the main polymer chain are not large in size and are regularly spaced, making BR an unique low-air, -moisture, and -gas permeability rubber.

PIB has a chemical backbone similar to that of BR, but does not contain double carbon–carbon bonds (only terminal unsaturation). Many of their characteristics are similar to those of BR (aging and chemical resistance, low water absorption, low permeability). The polymers of the isobutene family have very little tendency to crystallize. Their strength is reached by cross-linking instead of crystallization. The amorphous

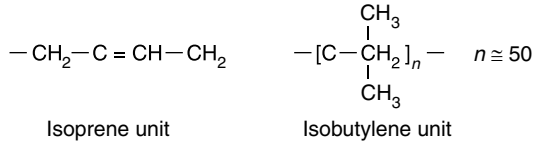


FIGURE 2.3 Chemical structure of butyl rubber.

structure of these polymers is responsible for their flexibility, permanent tack, and resistance to shock. Because the glass transition temperature is low (about −60°C), flexibility is maintained even a temperatures well below ambient temperature.

The structure of the isobutene-derived polymers corresponds to hydrocarbons and is mainly nonpolar, so poor adhesion to many surfaces is obtained. Thus, the addition of polar resins will improve adhesion.

The properties of BR and PIB depend on their molecular weight, degree of unsaturation, nature of the stabilizer incorporated during manufacture, and, in some cases, the chemical modification. It is common to produce halogenated forms of BR to increase polarity and provide a reactive site for alternate cure mechanisms [12].

Several partially cross-linked BRs are commercially available. The more tightly cross-linked grades are designated for butyl tapes. Various depolymerized BR and butyl/plasticizer blends are also available.

2.4.1.3 Styrene–Butadiene Rubber

SBR is mainly used for tire manufacturing and only a small amount is consumed in adhesives. SBR was developed during World War II in Germany and the United States as a substitute for NR, which was in short supply. SBR was produced by the emulsion copolymerization of butadiene and styrene and was called synthetic NR. After the War, when NR became available, the use of SBR declined because although its cost is low, the rubber lacks building tack and has poor cohesive and tensile strength, reduced hot tear strength, and lower elongation and resilience than NR. However, in the 1950s new polymerization procedures at low temperatures using redox catalysts and the development of solution polymerization using organolithium catalysts began to overcome those deficiencies, and SBR found applications in numerous adhesive formulations [13]. Currently, SBR adhesives are used as latices or as solid rubbers.

There are three steps in the manufacturing of SBR: polymerization, monomer recovery, and finishing. The polymerization step determines the basic characteristics of SBR, whereas the product form (latex or dry rubber, oil extended or not) depends on the finishing step.

SBR is produced by additional copolymerization of styrene and butadiene monomers in either an emulsion or a solution process. The styrene–butadiene ratio controls the T_g of the copolymer and, thus, its stiffness. T_g can be varied from −80°C (butadiene) to 100°C (styrene), and thus the higher the styrene content, the higher the stiffness of the copolymer. The chemical structure of SBR is given in Figure 2.4.

Because butadiene has two double carbon–carbon bonds, 1,2 and 1,4 addition reactions can be produced. The 1,2 addition provides a pendant vinyl group on the copolymer chain, leading to an increase in T_g. The 1,4 addition may occur in *cis* or *trans*. In free radical emulsion polymerization, the *cis*-to-*trans* ratio can be varied by changing the temperature (at low temperature, the *trans* form is favored), and about 20% of the vinyl pendant group remains in both isomers. In *solution polymerization* the pendant vinyl group can be varied from 10 to 90% by choosing the adequate solvent and catalyst system.

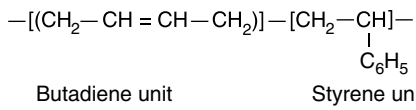


FIGURE 2.4 Chemical structure of SBR.

The formation of gel must be generally avoided. Gel formation is due to cross-linking of polymer chains during the growing step in emulsion polymerization. Gel content can be controlled by changing the temperature, adjusting the monomer to polymer conversion, and adding chain transfer agents. However, the gel portion in the SBR polymers is often sufficient to give good strength and creep resistance properties without cure (see also Chapter 1).

SBR are sold for adhesive manufacturing as latices or in solid form. Solid SBR is often preferred to NR because of its better thermal oxidative stability, higher abrasion resistance, and easier processability. Carboxylated styrene–butadiene rubber is a competitor to water-based acrylics (see also Chapter 8).

2.4.2 Resins

Tackifiers and modifiers are generally added to improve the adhesive performance of synthetic elastomers (see also Chapter 8). All resins added to an adhesive formulation modify their properties (viscosity, tack) and therefore these resins are also called modifiers. If the main aim of the addition of a resin is the increase of tack and adhesion properties, the resin acts as a tackifier (see also Chapter 8). (The term resin will be used in this chapter for both tackifiers and modifiers.)

Resins used in rubber-based PSA formulations have the following characteristics [14]:

1. Low molecular weight (M_w = 200–2000 g/mol) thermoplastic resins.
2. Viscous liquids to hard, brittle glasses at room temperature.
3. They are obtained from the derivatization of rosin or by polymerization of petroleum distillates, turpentine fractions, coal tar, and pure monomers.
4. Range from water-clear to dark brown or black color.
5. They are soluble in aliphatic and aromatic hydrocarbons and in many common organic solvents as well (see also Chapter 3).

In this section the rosins and rosin derivatives, coumarone–indene and hydrocarbon resins, polyterpene resins, and phenolic resins will be considered. The manufacture and structural characteristics of natural and synthetic resins will be first considered. In the second part of this section, the characterization and main properties of the resins will be described. Finally, the tackifier function of resins in rubbers will be considered.

The term resin is not well defined. Originally, it was applied to low-molecular-weight natural products, usually yellowish to brown in color, transparent to opaque, soft to brittle, easily fusible, tacky, amorphous material, soluble in most common organic solvents and insoluble in water. With the development of the chemical industry, the term

resin has also been applied to synthetic materials used as substitutes for natural resins or to materials with similar physical properties. According to International Standards ISO 472 and ISO 4618/3, resins are defined as "solid, semisolid, or pseudosolid organic materials that have an indefinite and often high relative molecular mass, and generally soften or melt over a range of temperatures." The resins have the following characteristics: medium molecular weight (lower than 10,000 g/mol); amorphous and complex structure; they do not exhibit a sharp melting point, but have a glass transition temperature; and they have a softening point (transition temperature from a pseudosolid to a plastic state; see also Table 8.7 in Chapter 8).

Resins can be divided into natural and synthetic products. Natural resins derive from vegetable or animal origin; typical representatives are rosins. Synthetic resins result from controlled chemical reactions and can be divided in two subgroups.

- Hydrocarbon resins produced by polymerization. These resins derived from coal tar, petroleum, and turpentine feedstock. Like natural resins, these resins are added to polymers to impart tack, flow, and hardness.
- Synthetic resins obtained by addition polymerization and polycondensation, which are intermediates in the synthesis of higher-molecular-weight plastics.

2.4.2.1 Manufacture and Structural Characteristics of Resins

2.4.2.1.1 Rosins and Rosin Derivatives

The resins more commonly used in rubber-based PSAs are rosin esters, particularly glycerol and pentaerythritol esters, as well as modified rosins by disproportionation and hydrogenation. The main aspects of rosin-based tackification technology include its manufacture (extraction) and chemistry.

Extraction of Rosin Rosin resins are produced from three types of rosin—gum, tall oil, and wood. Extensive details about rosin resin extraction and derivatization can be found in the book *Naval Stores. Production, Chemistry, Utilization* (Pulp Chemical Association, New York, 1989).

The extraction of gum rosin from the exudate of living pines was America's first widespread industry, which started in Nova Scotia in 1606. Normal resin ducts are found in the genera *Pinus, Picea, Psedotusga*, and *Larix*. They arise by producing vertical (longitudinal) and radial (horizontal) wounds in the log using a special tool called a hack. From the wounds, a slow flow of resin arises (which is greater in the first few hours after wounding a pine) and ceases after a few days. Resin flow stops because of tylosoid formation, crystallization of resin acids, or solidification of the resin [15]. Resin flow can be forced by spraying the wound with diluted sulfuric acid solution containing or not containing 5–8 wt% of 2-chloroethylphosphonic acid. The resin flows through a plastic or aluminum cup (iron cups causes oxidative darkening of the resin). The resin collected in the cups is transferred to a barrel for further processing. Before processing, the crude pine gum is cleaned by adding small amounts of oxalic acid to remove water-soluble impurities, iron contamination, and solid impurities (chips, bark). The resulting purified crude pine gum is distilled using a continuous stream of water to separate the turpentine (volatile essential oil

in the gum) from the rosin (the nonvolatile resinous material at the bottom of the distillation unit). The rosin is discharged and passes over cotton batting to remove unwanted solid material.

The wood rosin is obtained by solvent extraction of the stumps obtained from lumbering operations of pine trees. Stumps are first cleaned to remove sand, dirt, rocks, and other contaminants. Then, the stumps are reduced to relatively uniform-size chips using mechanical cutting devices. The chips are transported to the extraction equipment, where they are steamed to recover volatile terpene oils before solvent extraction begins. Several solvents can be used for rosin extraction but aliphatic petroleum hydrocarbon fractions with higher and narrower boiling ranges or methyl isobutyl ketone are generally used [16]. Extraction is generally carried out at elevated temperatures and under pressure (7–10 atm) for several hours. The extract solution is separated in continuous evaporators into three fractions: the recovered solvent (which is reused in the extraction process), volatile terpenes, and rosin. Rosin obtained from this extraction operation can be used without further operation, but very often color refining is done by adsorption or by using two immiscible solvents of different polarity. A typical yield of wood rosin in this process is about 70%.

The tall oil rosin is obtained from crude tall oil obtained from the kraft (sulfate) pulping of various coniferous trees in the paper manufacturing industry. During the kraft pulping process the fatty acids and the resin acids from the coniferous wood are saponified by the alkaline medium. On concentration of the resulting pulping liquor, the sodium soap of these mixed acids rises to the surface, where they are skimmed out. The crude tall oil is obtained by acidification of this material with sulfuric acid. Fractional steam distillation of the crude tall oil allows the separation of the tall oil fatty acids and the tall oil rosins [17].

Chemistry of Rosin All three types of rosin consist primarily of C_{20} monocarboxylic diterpene resin acids, the most common of which have the molecular formula $C_{20}H_{30}O_2$. In addition, rosins contain small amounts of neutral and other acidic components (e.g., fatty acids in tall oil rosin). The neutral components of rosins are diterpene alcohols, hydrocarbons, and aldehydes, and their content generally varies between 5 and 15%.

With very few exceptions, the pine resin acids belongs to four basic skeletal classes: abietane, pimarane, isopimarane, and labdane (Figure 2.5). The acids of the abietane, pimarane, and isopimarane series have an isopropyl or methyl/ethyl group in the carbon 13 position and a single carboxyl group in the carbon 18 position and differ only in the number and location of the double carbon–carbon bonds (the most common have two double carbon–carbon bonds). The acids of labdane series are less common and contain one carboxyl group in the carbon 19 position.

The structures and nomenclature for the common pine resin acids based on the abietane skeleton (abietic-type acids) are given in Figure 2.6. The abietic, neoabietic, palustric, and levopimaric acids differ only in the location of their two double bonds. All double bonds are endocyclic, except in neoabietic acid, where one is exocyclic.

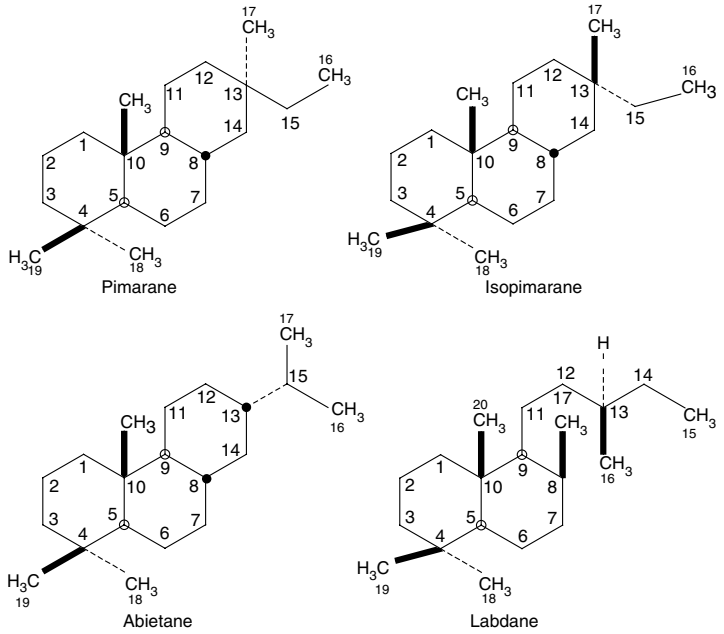


FIGURE 2.5 Principal monocarboxylic diterpene acids skeletons in rosins. The dotted line indicates that the chemical group is located below the plane.

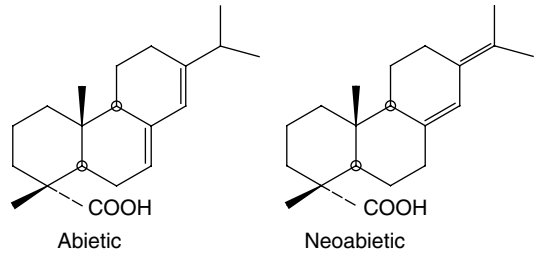


FIGURE 2.6 Common acids of the abietane skeletal class (abietic-type acids).

The common pine resin acids based on the pimarane and isopimarane skeletons (pimaric-type acids) are illustrated in Figure 2.7. Isopimaric and sandarcopimaric acids differ in the location of the double carbon–carbon.

The resin acids found in rosins are generally of the abietic and pimaric type. Rosins of various pine species differ in their content of abietic- versus pimaric-type acids. Rosins from species exhibiting high abietic-type acid compositions are preferred for the production of rosin derivatives. However, the differences in properties of rosins are often associated with their non-resin acid content instead of their chemical compositions. On

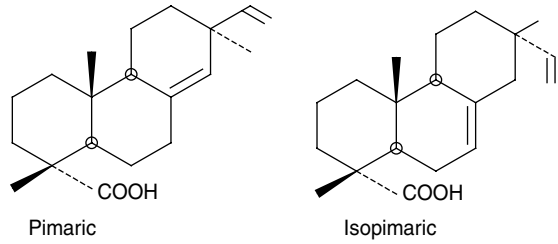


FIGURE 2.7 Common acids of the pimarane and isopimarane skeletal class (pimaric-type acids).

TABLE 2.3 Typical Composition (in percent of acid fraction) of the Common Resin Acids in Rosins Obtained from Different Sources

Resin Acid	Tall Oil Rosin	Wood Rosin	Gum Rosin
Pimaric	4.4	7.1	4.5
Sandarcopimaric	3.9	2.0	1.3
Communic	1.0	—	3.1
Levopimaric	—	—	1.8
Palustric	8.2	8.2	21.2
Isopimaric	11.4	15.5	17.4
Abietic	37.8	50.8	23.7
Dehydroabietic	18.2	7.9	5.3
Neoabietic	3.3	4.7	19.1

Source: Soltes, E.J., and Zinkel, D.F., Chemistry of rosin. In *Naval Stores. Production, Chemistry, Utilization*, New York: Pulp Chemical Association, 1989. With permission.

the other hand, the composition of rosins from different sources greatly differs [18]. Table 2.3 [18] illustrates a typical distribution of resin acids in rosins obtained from gum, tall oil, and wood sources. Most rosin utilization takes advantage of the carboxyl and olefinic functionalities of the resin acids.

The *olefinic functionality* produces instability of the rosin to oxidation, which causes undesirable yellowing. The conjugated double carbon–carbon bonds of the abietic acids leads to oxygen addition reactions and isomerization reactions. Rosin can be stabilized by removal of this conjugated unsaturation through hydrogenation and dehydrogenation reactions. Hydrogenation of the first conjugated double carbon–carbon bond is quite easy using a catalytic reaction with palladium or Raney nickel. After hydrogenation of the first double carbon–carbon bond, the residual carbon–carbon bond is hindered by steric effects and is more resistant to further hydrogenation. Hydrogenation at high pressure in the presence of a noble metal catalyst produces a fully hydrogenated product. Rosins can also be stabilized by heating at 200–300°C for several hours.

The most important single reactions produced in the *carboxyl functionality* of the resin acids are salt formation, Diels–Alder additions, and esterification. Other reactions,

such as disproportionation and polymerization, are less important. For some specific applications, rosins are subjected to a combination of these reactions.

Salt Formation. The resin acids have a low acid strength. The pK_s (ionization constants) values of resin acids are difficult to obtain, and values of 6.4 and 5.7 have been reported [19] for abietic and dehydroabietic acids, respectively. Resin acids form salts with sodium and aluminum. These salts can be used in detergents because of the micelle formation at low concentrations. Other metal salts (resinates) of magnesium, barium, calcium, lead, zinc, and cobalt are used in inks and adhesive formulations. These resinates are prepared by precipitation (addition of the heavy metal salt to a solution of sodium resinate) or fusion (rosin is fused with the heavy metal compound).

Esterification. The esterification of rosin provides important commercial products for the adhesive industry. Rosin esters are formed by the reaction of rosins with alcohols at elevated temperatures. Because the carboxyl group of the resin acids is hindered by attachment to a tertiary carbon, esterification with an alcohol can only be accomplished at elevated temperatures. This hindrance is, in turn, responsible for the high resistance of the resin acid ester linkage to cleavage by water, acid, and alkali.

Rosins are commonly combined with alcohols with more than one hydroxyl group, such as ethylene glycol and diethylene glycol (two hydroxyl groups), glycerol (three hydroxyl groups), and pentaerythritol (four hydroxyl groups). The reaction is carried out under an inert gas atmosphere (to prevent oxidation) at 260–280°C with or without a catalyst (boric acid, zinc oxide, lactic acid, etc); about 15–20% excess of alcohol with respect to the rosin is generally added. Water is a by-product of the reaction and its removal allows the reaction to be completed. Catalysts are generally used to speed the reaction and mainly to improve color and heat stability of the resulting rosin ester. Upon completion of esterification, some undesirable compounds (unreacted alcohol, traces of water, rosin oils) are removed under reduced pressure or steam sparging. In 1982, a new method to produce rosin esters at 30–40°C was established [20]. The method consisted of allowing a quaternary ammonium salt of resin acids to react with a polychloro-organic chemical, which also acts as solvent.

The rosin esters are clear and light in color. They are soluble in hydrocarbon solvents (solubility parameters of 8.4 to 9.0). They contain reduced acid number (about 10 for glycerol ester and about 15 for pentaerythritol ester) and are free of unsaturated alcohols (which would lower the softening point and decrease the water resistance of the rosin ester). The glycerol ester (usually called ester gum) remains one of the most important rosin esters that finds use in several adhesives formulations. The use of pentaerythritol esters imparts improved properties for varnishes because they have higher softening points and greater molecular weight than those of analogs glycerol esters.

Reduction to Alcohols. Copper chromite-catalytic hydrogenation of the methyl ester of rosin at 300°C under high pressure produced hydroabietyl alcohol. During hydrogenation, the carboxyl acid group is converted to a primary alcohol group, and the double carbon–carbon bonds of the parent resin acids are altered. The product is light in color and very resistant to air oxidation and finds application in adhesives as well as wetting agents and plasticizers.

2.4.2.1.2 Coumarone–Indene Resins

The first commercial coumarone–indene resin was manufactured in 1910. The basic material for the production of coumarone–indene resins is high-temperature coal tar. Coal tar is one of the by-products of coal carbonization. In the coking process, hard coal undergoes a pyrolytic conversion at temperatures of 1000–2000°C. The main product is coke but there are several by-products that are partly recoverable by condensation and extraction from the gases liberated during carbonization. Crude tar fraction accounts 3 wt % of the coal carbonization process. Distillation of coal tar renders less than 3 wt % coal-tar light oil, which is the main source for the manufacturing of coumarone–indene resins. This light oil fraction boils at 70–200°C and contains 10–40% unsaturated aromatics (Figure 2.8).

A typical composition of a coumarone–indene feedstream is 2 wt % styrene, 1 wt % α-methylstyrene, 30 wt % alkylbenzenes, 4 wt % vinyltoluenes, 5 wt % dicyclopentadiene, 7 wt % coumarone, 48 wt % indene, and 3 wt % methylindenes and methylcoumarones. According to the typical chemical composition of these resins, the coumarone content in the feedstock (and in the final resin) is very low compared with that for indene. Therefore, the use of the term polyindene resins would be more appropriate than coumarone–indene resins; however, this is not common practice.

During the high-temperature operations, intermolecular hydrogen transfer reactions occur, transforming some indene to indane. The high indane concentration in the resin feedstock causes low yield and poor quality in the polymerization process. The indene loss can be reduced by decreasing temperature and residence time during distillation.

The raw material must be washed to remove impurities. Diluted sodium hydroxide allows the removal of phenols and benzonitrile, and diluted sulfuric acid reacts with pyridine bases. The resulting material is distilled to concentrate the unsaturated compounds (raw feedstock for coumarone–indene resin production) and separate and recover interesting nonpolymerizable compounds (naphthalene, benzene, toluene, xylenes). Once the unsaturated compounds are distilled, they are treated with small

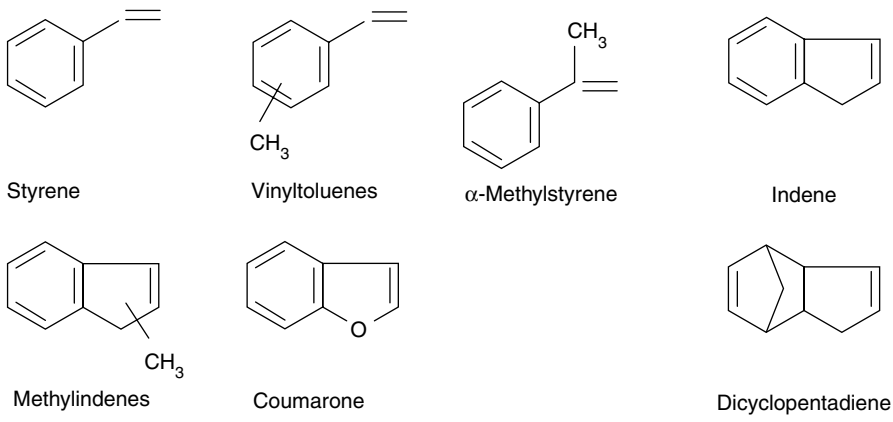


FIGURE 2.8 Chemical structure of components in coumarone–indene resins.

amounts of sulfuric acid to improve color; activated carbons or clays can be also used. The resulting material is subjected to polymerization. It is important to avoid a long storage time of the feedstock because oxidation processes can be easily produced, affecting the polymerization reaction and the color of the coumarone–indene resins.

Coumarone–indene resins were produced by adding sulfuric acid to the stirred feedstock at 20–35°C, taking care to produce a good dispersion of sulfuric acid to avoid scorching (dark-colored resins are obtained) and to control the temperature (it is a strongly isothermal reaction). Today, the coumarone–indene resins are obtained using a BF_3/phenol mixture as initiator (see below).

The polymerization processes of coal tar and petroleum fraction (from which aromatic hydrocarbon resin are obtained) are similar. The process is extensively described in *Hydrocarbon Resins* by R. Mildenberg, M. Zander, and G. Collin (VCH, Weinheim, 1997). There are three basic steps in the polymerization of coumarone–indene and hydrocarbon resins:

- *Initiation*. A Friedel–Craft acid (hydrochloric acid, water, phenol) is used as an initiator, together with a proton source ("coinitiator;" BF_3 or $AlCl_3$ are the most common). The mixture produced a cation, which is the true initiating species.
- Propagation.
- *Termination*, which can be achieved using nucleophiles (alcohols, ammonia, amines, alkalis, water).

Several reaction parameters affect the composition of the coumarone–indene resins. Therefore, in the presence of $AlCl_3$ the resins have a higher molecular weight than those produced in the presence of BF_3. The high initial concentration of the initiator produces coumarone–indene resins with lower molecular weight. Finally, the molecular weight and the yield of the resin increase with increases in the temperature of the reaction.

After deactivation and removal of the initiating system, the coumarone–indene resin is separated from solvent and low-molecular-weight materials by vacuum distillation. Removal of the low-molecular-weight materials is important because they produce a strong odor, act as softeners, and cause an undesirable decrease in softening point. Therefore, at this stage the softening point of the coumarone–indene resins is adjusted. Finally, stabilizers are added to the liquid resin while it is still hot to inhibit further oxidation (which causes discoloration and odor).

One of the key properties of coumarone–indene resins is the softening point. This is determined by careful selection of the feedstock, manufacturing process, level of constancy in temperature during reaction, and concentration of initiating system. Cuomarone–indene resins obtained using this procedure have softening points from liquid to 170°C and Gardner color of 5 to 9.

The structural element of a coumarone–indene resin is relatively similar to that for aromatic hydrocarbon resins, because they differ only in the proportion of indene-type structures, which are present in higher concentrations in the coumarone–indene resins. The main monomers in the aromatic resins are styrene and indene. Styrene produces the atactic conformation of the resins, whereas indene introduces rigidity to the polymer chain. A typical structure element of an aromatic resin is illustrated in Figure 2.9.

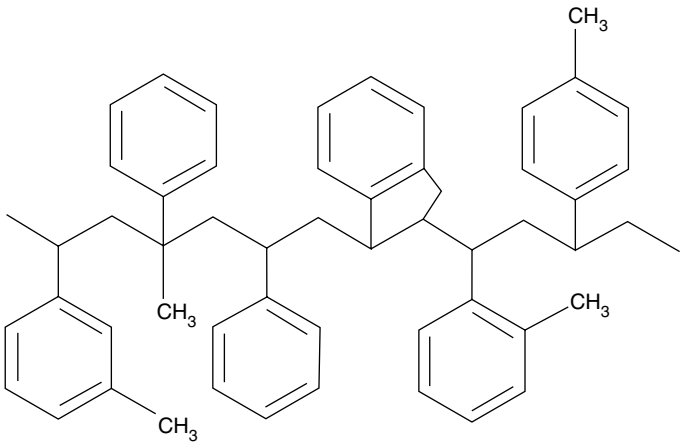


FIGURE 2.9 Structural element of an aromatic hydrocarbon resin.

Coumarone–indene resins can be modified to match specific properties. Some of the most common modifications in those resins are the following:

1. *Styrene-modified coumarone–indene resins*. These are intended for formulating floor tiles to avoid indentations produced by the pressure of women's heeled footwear. The modification is produced by copolymerization of the coumarone–indene resin with 15% styrene using normal polymerization conditions. The resulting resins have higher solution and melt viscosity than the unmodified coumarone–indene resin.
2. *Phenol-modified aromatic resins*. Coumarone–indene resins are essentially nonpolar in nature. The reaction with phenol allows the introduction of hydroxyl groups, which provide polarity. About 10–15% phenol is incorporated in the resin and it is completely reacted (e.g., there is no free phenol). These phenol-modified resins can be used in adhesive formulations (e.g., floor coverings) because of their adequate solubility (in alcohols, glycols, esters, and ketones) and compatibility. The most common grade has a softening point of 90°C.

2.4.2.1.3 Hydrocarbon Resins

Little literature exists concerning the manufacturing, chemistry, and properties of hydrocarbon resins. One of the few contributions in this area is the book by R. Mildenberg, M. Zander, and G. Collin, *Hydrocarbon Resin* (VCH, Weinheim, 1997).

Separation of Raw Feedstock The pyrolysis of petroleum feedstream is carried out at 650–900°C at normal pressure in the presence of steam. The so-called steamcracking process involves carbon–carbon splitting of saturated, unsaturated, and aromatic

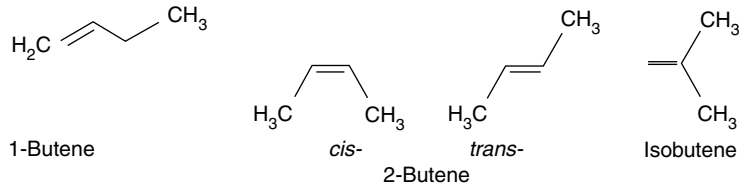


FIGURE 2.10 Chemical structure of components in aliphatic hydrocarbon resins.

molecules. The following steam cracker fractions are used as raw materials to produce hydrocarbon resins:

- C_5 *streams*. They contain linear and cyclic olefins, such as isoamylene, isoprene, piperylene, C_5 paraffins, and cyclopentadiene (Figure 2.10). *Aliphatic hydrocarbon resins* can be obtained from the unsaturated components of this fraction. Cyclopentadiene tends to dimerize during operation and is deposited at the bottom of the reactor (heat-soaking favors deposition). The dicyclopentadiene (DCPD) is removed from the reactor and used to produce the DCPD resins. Finally, isoprene is separated from piperylene concentrate, which is the feedstock used to manufacture aliphatic hydrocarbon resins.
- C_8/C_9 *streams*. They contain unsaturated aromatics (e.g., styrene, indenes). *Aromatic hydrocarbon resins* can be obtained from these streams. Benzene, toluene, and xylene are drawn off from the stream and a C_9 material containing unsaturated compounds with a boiling range 160–200°C is obtained. This C_9 resin material has the following typical composition: 2 wt % styrene, 4 wt % α-methylstyrene, 20 wt % vinyltoluene, 6 wt % dicyclopentadiene and codimers, 20 wt % indene, 5 wt % methylindenes, 5 wt % naphthalene, and 38 wt % other nonreactive aromatics.

  A further source of C_9 material is coal tar. Structures of the two resins precursors are roughly similar, except for the presence of small quantities of coumarone in the coal tar feedstream. There is a significant difference in the concentrations of individual monomers: Coal tar-based raw material is richer in indene (styrene:indene ratio = 1:7) than the petroleum-based feedstream (styrene:indene ratio = 1:1);
- C_4 *streams*. They contain olefins, mainly isobutenes, which by cationic polymerization produce polybutene oligomers. Low-molecular-weight polybutene resins are mainly composed of isobutene (15–30 wt %), 1-butene (10 wt %), and *cis* and *trans* 2-butenes (10–15 wt %).
- *DCPD streams*. DCPD concentrates are generated by dimerization of cyclopentadiene (Figure 2.11) in the heat-soaking process of the effluents in the C_8/C_9 stream-cracking of petroleum feedstock. DCPD resins can be obtained from these streams.

Polymerization of Raw Feedstock *Aliphatic Hydrocarbon Resins*. Raw feedstock contains straight-chain and cyclic molecules and mono- and diolefins. The most common

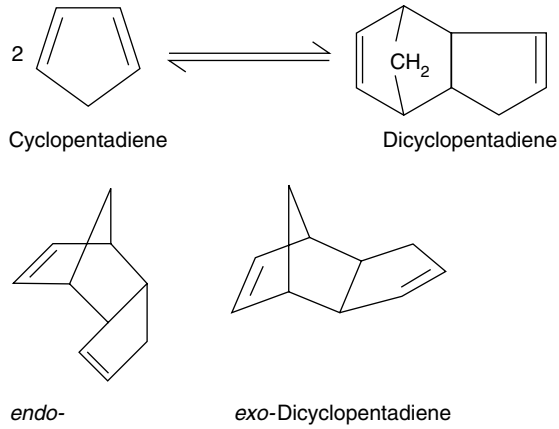


FIGURE 2.11 Chemical structure of components in dicyclopentadiene resins.

initiator in the polymerization reaction is $AlCl_3$/HCl in xylene. The resinification consists of a two-stage polymerization in a reactor at 45°C and high pressure (10 MPa) for several hours. The resulting solution is treated with water and passed to distillation to obtain the aliphatic hydrocarbon resins. Several aliphatic hydrocarbon resins with different softening points can be adjusted.

- Unmodified aliphatic hydrocarbon resins: softening point = 80–100°C; Gardner color = 3.5–7
- Modified aliphatic hydrocarbon resins
- Cyclic-modified aliphatic hydrocarbon resins: softening point = 115°C; Gardner color = 5
- Aromatic-modified aliphatic hydrocarbon resins: softening point = liquid to 90°C; Gardner color = 5–9
- Cyclic/aromatic-modified aliphatic hydrocarbon resins: softening point = 95°C; Gardner color = 3

The structure of aliphatic resins is difficult to determine because they contain straight-chain and cyclic structures [21].

Aromatic Hydrocarbon Resins. The polymerization procedure and variables in the reactions of the aromatic hydrocarbon resins are similar to that for coumarone–indene resins. However, the C_9 feedstreams used in the polymerization of the aromatic hydrocarbon resins do not contain significant amounts of phenols or pyridine bases, so they are submitted directly to fractional distillation. Distillation produced more by-products than light coal-tar oils. The aromatic hydrocarbon resins obtained have softening points between liquid and 125°C and Gardner color of 6 to 11. By changing the distillation conditions, aromatic hydrocarbon resins with softening points between 65 and 170°C and Gardner color of 5 to 10 can also be obtained.

DCPD Resins. In contrast with the polymerization process to produce aliphatic and aromatic resins, the polymerization of DCPD is carried out by heating (it is a very exothermal reaction, so temperature must be carefully controlled). The addition of

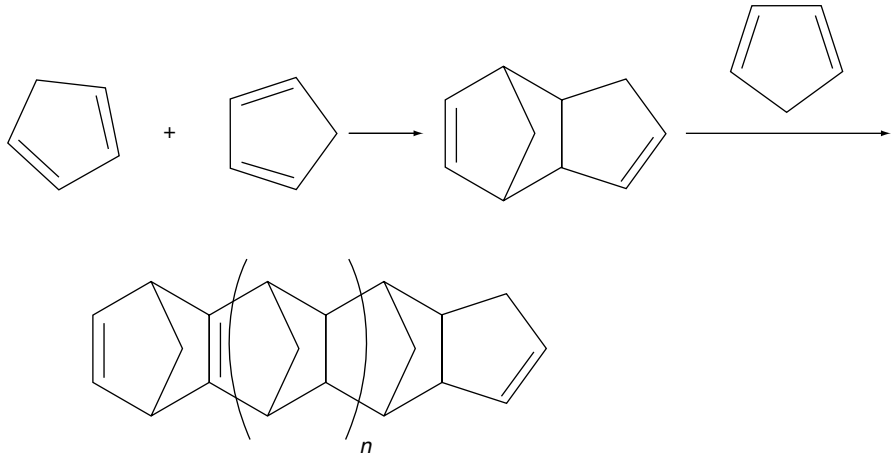


FIGURE 2.12 Structural element of a dicyclopentadiene resin. (From Mildenberg, R., Zander, M., and Collin, G., *Hydrocarbon Resin*, Weinheim, VCH, 1997. With permission.)

aromatic unsaturated species (e.g., styrene, vinyltoluene) to DCPD is typical, because the heat of reaction is reduced and allows appropriate modification of the properties in the final resins. The polymerization of DCPD streams is a pressure/temperature reaction that does not require a catalyst. After the DCPD stream is blended with a high flash point solvent (xylene, mineral spirits 140/160, naphtha), pressure is applied with preheating at about 60°C. The polymerization is produced in 15 h by increasing the temperature in two or three steps until a temperature between 200 and 280°C is reached. The resulting materials are distilled and DCPD resins with softening points between 30 and 120°C, Gardner colors of 5 to 6, and iodine numbers from 95 to 175 are obtained.

The basic structure of the DCPD resins is given in Figure 2.12 [22].

The highly unsaturated DCPD resins are generally modified to improve their performance in the adhesives and printing ink industry. Three modifications are generally produced.

1. Hydrogenated DCPD resins. Hydrogenation of resins leads to very light-colored products and also produces remarkable stability to light and heat. Hydrogenation of DCPD resins is generally carried out under pressure and high temperature in the presence of a nickel catalyst for about 3 h. The resulting hydrogenated DCPD resins have softening points of 80–130°C and Gardner color below 1.
2. Maleic anhydride-modified DCPD resins. Heating of the DCPD resin with 10% maleic anhydride for 3 h at 200°C produces a resin with softening point of 180°C and acid number of 53.
3. Rosin-modified DCPD resins. The DCPD resin is heated with 30% rosin ester.

Polybutene Resins. These liquid resins are obtained by cationic polymerization of petroleum C_4 streams in the presence of $AlCl_3$ at relatively low temperature. Temperature and $AlCl_3$ concentration are important factors because they influence the molecular

weight and viscosity of the final resin. After the reaction, the mixture is deactivated with water, methanol, ammonia, or aqueous sodium hydroxide. The organic layer is separated and distilled to remove the solvent and unconverted material.

2.4.2.1.4 Polyterpene Resins

Terpene resins are obtained from natural terpene monomers obtained from naval stores, paper pulp production, and citrus juice production. Terpenes are found in almost all living plants, and pine trees are the most important source.

Gum turpentine is obtained from wounding living trees to yield an exudate containing turpentine and rosin. Turpentine is separated from the rosin by continuous steam distillation and further fractionation. Wood turpentine comes from the extraction of stumps of pine trees using naphtha and subsequent separation of the rosin and turpentine by fractional distillation. Tall-oil turpentine is a by-product of the kraft sulfate paper manufacture. Terpenes are isolated from the sulfate terpentine and separated from the black digestion liquor. The composition of turpentine oils depends on its source, although α-pinene and β-pinene are the major components.

Crude turpentine is distilled to obtain the refined products used in the fragrance and flavor industry. Only the unsaturated mono- and bicyclic terpenes are of interest for resin production. These are mainly α-pinene, β-pinene, and dipentene (D,L-limonene) (Figure 2.13). D-Limonene is obtained by extraction of peel in citrus fruits.

Polymerization of terpene monomers is carried out at 30–50°C using $AlCl_3$ as an initiator and xylene or toluene as the diluting solvent. The reaction must be carried out under an inert gas atmosphere to avoid oxidation of the polyterpenes. The initiating system is deactivated by adding water under vigorous stirring. After phase separation, the organic layer is separated and submitted to vacuum distillation to take off the diluent. At this stage the softening point of the resin can be adjusted by removal of the low-molecular-weight dimers and trimers. Finally, antioxidants must be added for protection against oxidation.

The typical structure of the polyterpene resins is given in Figure 2.14 [22].

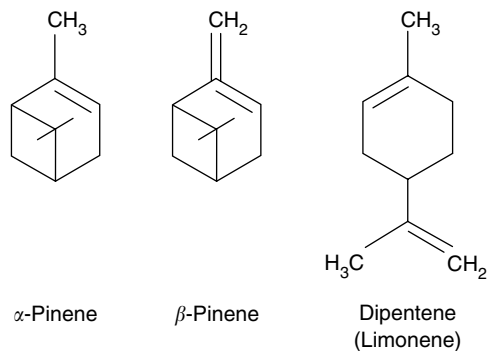


FIGURE 2.13 Chemical structure of components in polyterpene resins.

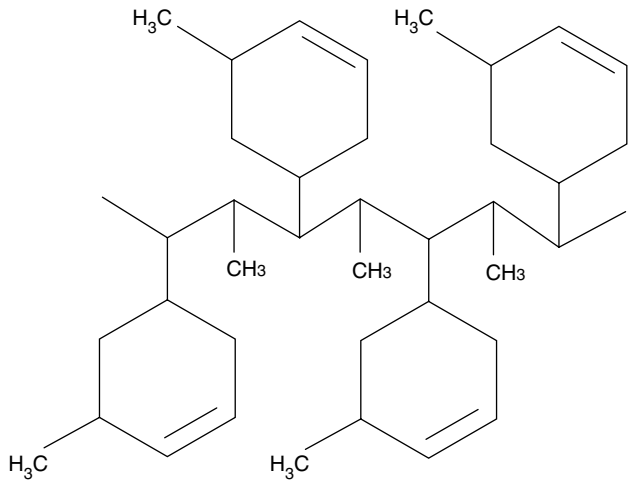


FIGURE 2.14 Structural element of a polyterpene resin. (From Mildenberg, R., Zander, M., and Collin, G., *Hydrocarbon Resin*, Weinheim, VCH, 1997. With permission.)

2.4.2.1.5 Resins from Pure Monomers

Some colorless resins can be produced from pure unsaturated monomers, such as styrene, α-methylstyrene, and vinyltoluenes. These monomers are used individually or as blends with terpenes or unsaturated aliphatics.

The raw feedstock used to produce these resins are obtained using synthetic routes.

- Styrene is obtained by alkylation of benzene with ethylene in the presence of aluminum chloride as a catalyst, followed by dehydrogenation.
- α-Methylstyrene is obtained as a by-product in the production of phenol by the oxidation of cumene to hydroperoxide and subsequent splitting by acids.
- Vinyltoluenes are manufactured by the alkylation of toluene followed by dehydrogenation.

Production of these resins is similar to that for the coumarone–indene resins. Because the raw material does not contain impurities, a small amount of initiating system can be used.

2.4.2.2 Characterization and Main Properties of Resins

The properties of the resins provide information about their suitability for specific applications and their main characteristics are the aliphatic/aromatic character and the unsaturation degree.

Commercial data sheets generally provide the following properties for the resins:

- Softening point
- Color
- Degree of unsaturation

- Acid number
- Saponification number
- Density
- Ash content
- Odor

However, other properties are also important in adhesive performance, such as solubility, compatibility, chemical and thermal stability, viscosity, and molecular weight and molecular weight distribution.

Softening Point. The resins are noncrystalline amorphous materials that soften gradually over a range of temperatures. Therefore, the softening point is controlled by the average molecular weight of the resin. The softening point is also related to the intrinsic viscosity, hardness, and brittleness of resins.

The softening point is defined as the temperature at which the resin flows under a given load on heating. Several standard methods have been proposed to determine the softening point of resins.

- *Ring and Ball Method* (R&B): ASTM D 3461-76, DIN ISO 4625. This method is the most frequently used to determine the softening point of resins. Figure 2.15 illustrates the experimental device used to determine the R&B softening point. The resin is melted into a metal ring and left to cool. The ring is placed in a special metallic device, which is placed into a water or glycerol bath. A steel ball of given diameter and mass is placed on the ring and the bath is heated at a given rate. The temperature at which the ball forces the softening resin downward is noted as the softening point.
- *Krämer–Sarnow Method*: DIN 53 180. This is the oldest method used to determine the softening point of resins and is relatively similar to the R&B method. Instead of a ring, a small glass tube that is open at both ends is used and the load is a small mercury drop. The softening point is obtained as the temperature at which the mercury drop breaks through the softening resin and falls.
- *Mettler Softening Point Method*: ASTM D 3461-76. This is the most recent method. This automatic method measures the temperature at which the resin flows out of a sample cup under its own weight. The temperature is recorded when the first drop crosses the light path of a photocell (Figure 2.16). This method is quite accurate and reproducible.
- *Plate–Plate Stress Rheometer Test*. The resin is placed between the two steel plates of a stress-controlled rheometer, maintaining a gap larger than 0.5 cm. The upper plate is oscillated at a given frequency, whereas the lower plate is heated. The variation of the storage and loss moduli as a function of the temperature is monitored. The softening temperature can be estimated from the temperature at the cross-over between the two moduli [25].

Although not widely used, other methods to determine the softening point exist, such as the capillary method, the flow point, the drop point, and the Kofler method. The different methods provide different softening point values. In general, the R&B method provides the highest softening point, whereas the Mettler method provides the lowest

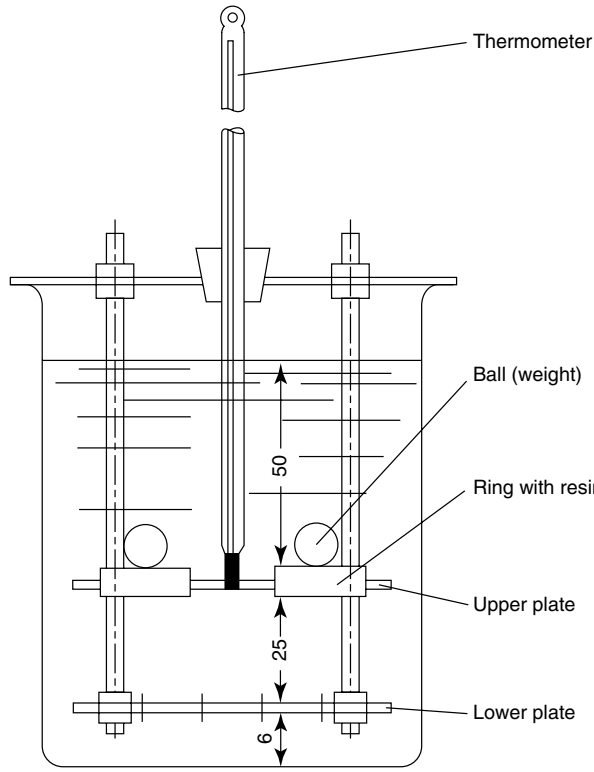


FIGURE 2.15 Determination of R&B softening point (numbers in millimeters). (From Mildenberg, R., Zander, M., and Collin, G., *Hydrocarbon Resin*, Weinheim, VCH, 1997. With permission.)

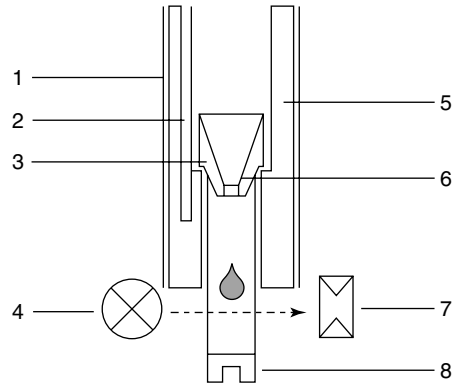


FIGURE 2.16 Determination of the Mettler softening point. 1. Heating element. 2. Platinum resistance thermometer. 3. Sample. 4. Light source. 5. Furnace. 6. Sample cup. 7. Photo cell. 8. Collector sleeve. (From Mildenberg, R., Zander, M., and Collin, G., *Hydrocarbon Resin*, Weinheim, VCH. 1997. With permission.)

softening point for a given resin. Therefore, both the softening point value and the method used for its determination should always be given. In general, manufacturers supply resins with a tolerance of about 3°C in the R&B softening point method. A comparative examination of the methods for resin softening point characterization is given in Chapter 8.

Rubber-grade resins are mostly in the softening point range of 70–100°C R&B. A deviation of 5–10°C in softening point may cause problems. The softening point of a resin affects the adhesive properties. Hence, for pressure-sensitive rubber adhesives a decrease in the softening point of the resin produces tackier and less cohesive strength in the adhesive.

Color. The color of resins ranges from water-white to dark brown. Color may be an important factor in resin choice depending on end use. Pale colors are necessary in some types of adhesives, whereas darker colors may be tolerated in rubber formulations, especially where carbon black filler is incorporated. Medium-color resins can be used in most adhesive formulations.

The color can be determined using various methods such as the Gardner, Barrett, iodine color number or U.S. Colophonium standard methods. Usually, the Gardner or Barrett standards are used. A comparison between the different methods to determine the color of resins is given in Table 2.4 [26]. In both methods, the color is evaluated in resin solutions. A 50% resin solution in toluene is used as the Gardner standard, and a solution of 2 g resin in 25 mL toluene is used in the Barrett standard. These solutions are made in calibrated tubes and are compared with a set of standard color disks.

On the other hand, not only initial color but also color change (discoloration) of the resin under ultraviolet (UV) light and heat is important. The color retention of a resin is

TABLE 2.4 Comparison of Color Standard for Resins

Barrett	Gardner	Iodine Number	U.S. Colophonium Standard
0.5	6	10	X
	7	12	WW
	8	15	WG
	8.5		N
1	9	20	M
	10	25	K
	11	40	I
	12	70	H
	12.5		G
1.5	13	105	
	14	145	F
	15	190	
	16	245	E
2	17	300	
2.5	18	445	D
3		2000	

Source: Mildenberg, R., Zander, M., and Collin, G., *Hydrocarbon Resin*, Weinheim, VCH, 1997. With permission.

related to its chemical stability and increases as the degree of nonaromatic conjugated unsaturation of the resin molecule decreases. Thus, for rosins a high level of abietic-type resin acids lead to relatively unstable resins. Hydrogenation and disproportionation, as well as esterification, provide improved stability and color retention to rosins.

Odor. This aspect is important in resins derived from natural sources. Rosins based on wood and gum rosin retain trace quantities of terpenes and have a "piney" odor. Tall oil rosins retain the typical sour odor of the rosin. Odor can be removed by steam sparging under vacuum before or during esterification of the rosins. The addition of odor masks can also be performed.

Degree of Unsaturation. Unsaturation accounts for the existence of double carbon–carbon bonds in resins. It is generally indicated by the bromine or iodine number. Both methods are based on the halogen addition to the double carbon–carbon bonds.

- Bromine number: ASTM D 1159-84. The bromine number is defined as the amount of bromine in grams accepted by 100 g of resin. Typical values are as follows.
  - Nonreactive resins: 10–45 g Br_2/100 g resin.
  - Reactive resins: 55–75 g Br_2/100 g resin.
  - Highly reactive resins: 65–100 g Br_2/100 g resin.
- Iodine number: ASTM 1959–69. The iodine number is defined as the amount of iodine in grams accepted by 100 g of resin.

Because of the different reactivities of bromine and iodine, the numbers cannot be compared. The bromine or iodine number does not necessarily correlate with the reactivity of the resin, for instance, in the aging process. However, within a given DCPD resin series of the same structure, relative comparison can be made.

Acid Number (ASTM D 974-80, DIN 51 558). The acid number is defined as the amount of potassium hydroxide in milligrams required to neutralize 1 g of resin under fixed conditions.

The acid number is mainly defined for rosins and rosin-derived resins and for phenol-modified resins. Standard hydrocarbon resins have zero acid number because of the absence of functional groups. However, the acid number allows for the control of deterioration by oxidation with formation of the carbonyl and carboxyl groups in hydrocarbon resins. Typical acid number values of different resin types are as follows.

- Hydrocarbon resins: 0.1 mg KOH/g resin
- Phenol-modified resins: 0.3–0.5 mg KOH/g resin
- Rosins: 150–175 mg KOH/g resin
- Rosin esters: 50–75 mg KOH/g resin

For rosins and rosin esters, the products with high acid numbers are the most susceptible to oxidation and have inferior viscosity stability and color stability in adhesive formulations. Thus, when stability properties are essential in adhesives, rosin esters rather than high-acid-number rosins are used. However, the high-acid-number resins are polar and display better adhesion to polar elastomers and polymeric surfaces.

Saponification Number (DIN 51 559). The saponification number is indicative of the presence of ester groups in a resin. The saponification number is defined as the

consumption of potassium hydroxide in milligrams by 1 g of resin under standardized conditions. The saponification number is important for rosin derivatives.

Density. Density is the mass of unit volume at a given temperature. For solid resins, density is evaluated according to DIN 51 757 at 20°C, whereas for liquid resins DIN 1995 U2 at 20°C is more appropriate. Densities of resins usually are in the range of 0.88 to 1.15 g/cm^3.

Ash Content (DIN 52 005). The unwanted presence of inorganic impurities due to incorrect filtration of neutralization residues and rust contaminants is undesirable because it may contribute to premature aging. Ash determination provides some interesting information. In general, most resins have ash content lower than 0.1%.

Glass Transition Temperature (T_g). Resins are amorphous polymers exhibiting a glass transition due to the reduction of molecular mobility by the collapse of free volume with falling temperature. Differential scanning calorimetry (DSC) is an appropriate technique to obtain T_g values of resins. In general, resins exhibit a relaxation process near the glass transition, which makes it difficult to quantify the T_g value [27]. Removal of the thermal history of the resin during a first heating run in the DSC equipment is recommended. After a sudden cooling down of the melted resin to low temperatures, a second run is carried out, from which the T_g value can be easily obtained.

T_g values of resins (30–90°C) are higher than those of rubbers (−70 to −30°C), so the addition of resin can be used to raise the average T_g of the rubber-based formulations (see also *Applications of Pressure-Sensitive Products,* Chapter 8).

Solubility. Generally, resins are soluble in most common organic solvents, especially aromatics, esters, and chlorinated solvents. They are insoluble in water. Solubility depends on resin type, average molecular weight, and distribution. In general, higher softening point resins are less soluble than lower softening point types.

The solubility of resins can be predicted in a similar way to the solubility of polychloroprene rubbers in solvent mixtures (see Section 2.5.5) by means of solubility diagrams [plots of the hydrogen bonding index (γ) against the solubility parameter (δ)]. A simpler way to determine the solubility of resins is the determination of the cloud point, the aniline, and the mixed aniline points.

- *Cloud Point.* Measures the solubility/compatibility of a resin with solvents. The value reported is the temperature at which a specific mixture of a resin and a solvent or solvents blend gives a cloudy appearance, having been cooled from a temperature at which the mixture was clear. Commonly, a test tube of a given diameter is used and the temperature is noted when the lower end of the thermometer, placed at the bottom of the tube, disappears. Resins with cloud points below 0°C are commonly regarded as soluble and cloud points greater than 70°C indicate poor solubility/compatibility.

  White spirit with various aromatic contents is a widely used solvent in the determination of cloud point, but other solvents or solvents mixtures are also used.
- *Aniline and Mixed Aniline Point* (DIN 51 775 modified). This is similar to the cloud point test except that the solvent is aniline, a very polar liquid. The aniline point is defined as the temperature at which a mixture of equal parts of aniline and the resin show the beginning of phase separation (i.e., the onset of clouding).

Phase separation for aromatic resins occurs between 15°C and below zero; for resins with intermediate aromaticity, it lies between 30 and 50°C; and for non-aromatic resins, it is 50 to 100°C.

Sometimes the mixed aniline point is used. This is similar to the aniline point except that the solvent is a mixture of one part of aniline and one part *n*-heptane. The problem with both procedures is that precipitation of resins can be produced before the cloud is generated.

One important factor influencing the solubility of rosin derivatives is their tendency to crystallize. Initially, a rosin product may appear to be soluble in a given solvent, but upon standing, the rosin will crystallize out of the soluble solution. This tendency of rosin to crystallize can be overcome by derivatization, mainly esterification.

Compatibility. A clear definition of compatibility is rather difficult. Compatibility has been defined as the ability of two or more materials to exist in close and permanent association for an indefinite period without phase separation and without adverse effect on each other [28]. Compatibility is easily recognized in solvent-borne adhesives as a homogeneous blend of materials without phase separation. Compatibility is understood as a clear transparent mixture of a resin with a given polymer. But compatibility is a more complex thermodynamic phenomenon that can be evaluated from specific physical properties, such as the glass transition temperature. For instance, the T_g measurements allow the determination of the compatibility of blends in rubber–resin blends [29]. A compatible blend will exhibit only one T_g with an intermediate value between the T_g values of the rubber and the resin, whereas an incompatible blend will exhibit two T_g values.

In general, resins are compatible with a large number of materials (oils, plasticizers, polyethylene waxes, rubbers). Compatibility depends on resin type, molecular weight and its distribution, resin structure and configuration, and applications requirements.

The most common method to measure the compatibility of resins with other substances is to dissolve both materials in a mutually compatible solvent and to cast a film on a glass slide. After solvent evaporation, a compatible system yields a clear film, whereas incompatibility results in an opaque film. A more accurate procedure is to melt the resin under a phase microscope, and compatibility is observed on the film after cooling.

A more quantitative estimation of compatibility can be obtained with the solvent cloud point test. The solvent cloud point is based on the idea that resins will be compatible with elastomers of similar chemical nature. Thus, aliphatic resins will be effective tackifiers for aliphatic elastomers, such as natural rubber, whereas aromatic solvents are needed for aromatic elastomers, such as SBR. Solvent cloud point tests are carried out in three solvent systems that represent aliphatic, aromatic, or polar systems [23].

- Aliphatic system: odorless mineral spirit
- Aromatic system: methylcyclohexanone/aniline (MMAP)
- Polar system: diacetone alcohol/xylene

Rosin esters demonstrate low cloud points and would have wide compatibility with most elastomers. Aliphatic hydrocarbon resins, however, will only be compatible with aliphatic elastomers (e.g., natural rubber).

In general, fully compatible resins are desirable. However, there are many applications in which borderline compatibility is tolerated, and in some cases, borderline compatibility or controlled incompatibility may enhance tack in adhesive systems. On the other hand, a resin with a borderline compatibility in combination with an oil or plasticizer in an adhesive formulation will result in phase separation and therefore the migration of the oil or plasticizer to the adhesive surface is favored.

Viscosity. Solvent viscosity of resins is influenced by the concentration of the resin, the softening point, the molecular weight distribution, the chemical composition of the resin, and the type of solvent. The higher the resin concentration, the higher the viscosity. For a given concentration, solution viscosity depends on the softening point of the resin.

The softening point is related to the average molecular weight of a given resin, but resins with similar softening point may have different molecular weight distributions and hence different viscosity in solution. The molecular weight distribution has a tremendous influence on resin solution viscosity. The narrower the molecular weight distribution, the higher the viscosity of the resin solution.

2.4.2.3 Tackifier Function of the Resins

To produce a suitable rubber-based PSA, the following aspects are required: (i) tack and wetting properties, (ii) adhesive strength, and (iii) cohesive strength.

Adhesive strength refers to the bond produced by the contact of an adhesive to a surface. It used to be measured by peeling tests. The ultimate strength depends on temperature, applied pressure, and time of contact (see also *Fundamentals of Pressure Sensitivity,* Chapter 7, and *Applications of Pressure-Sensitive Products*, Chapter 7).

Cohesive strength is the internal strength of an adhesive or the ability of the adhesive to resist splitting. Unlike tack and adhesion strength, cohesive strength is not influenced by the substrate (see also *Fundamentals of Pressure Sensitivity,* Chapter 8, and *Applications of Pressure-Sensitive Products*, Chapter 8).

Tack is difficult to define. In adhesive technology, tack can be defined as the property of a material that enables it to form a bond of measurable strength immediately upon contact with another surface, usually with no or low applied pressure (see also *Fundamentals of Pressure Sensitivity*, Chapter 6, and *Applications of Pressure-Sensitive Products*, Chapter 8). Therefore, tack is associated with instantaneous adhesion and differs from final strength, which requires a longer time. Tack is a function of the rheological properties of the adhesive and of the surface energies of the adhesive and the bonded substrate surface. Tack is sensitive to variations in temperature, pressure, rate of application and removal pressure, and contact time. Measurement of tack is difficult and several procedures have been suggested [14]. However, none of them is completely satisfactory, although the probe tack seems to be the most widely accepted.

- *Finger test*. This is the simplest test. A small amount of adhesive is placed on a finger and pressed against the thumb. The difficulty in separating the finger and thumb provides a rough estimation of tack.
- *Rolling ball*. A small steel ball with a specific weight and diameter is rolled down an incline plane onto a thin film of adhesive placed at the bottom. The

distance the ball rolls on the adhesive film before stopping is a measure of the tack (the longer the distance, the lower the tack; see also *Applications of Pressure-Sensitive Products*, Chapter 8).

- *Probe tack*. A probe (flat or not) is contacted with an adhesive film at a given pressure and dwell time. The force required to remove the probe from the adhesive is a measure of tack [30] (see also *Applications of Pressure-Sensitive Products*, Chapter 8).

Tackifying resins enhance the adhesion of nonpolar elastomers by improving wettability, increasing polarity, and altering the viscoelastic properties (Chapter 8). Dahlquist [31] established the first evidence of modification of the viscoelastic properties of an elastomer by adding resins and demonstrated that the performance of PSAs was related to creep compliance (Dahlquist's criterion). Later, Aubrey and Sherriff [32] demonstrated that a relationship between peel strength and viscoelasticity in natural rubber–low-molecular-weight resins blends existed. Class and Chu [33] used the dynamic mechanical thermal analysis measurements to demonstrate that compatible resins with an elastomer produced a decrease in the elastic modulus at room temperature and an increase in the tan δ peak (which indicated the glass transition temperature of the resin–elastomer blend). Resins that are incompatible with an elastomer caused an increase in the elastic modulus at room temperature and demonstrated two distinct maxima in the tan δ curve.

The modification of an elastomer by a low-molecular-weight resin is determined by the compatibility (or solubility) of the resin in the elastomer. Compatibility is necessary to generate tack, but it does not ensure that desired adhesive properties will be obtained. The adhesive performance of a resin–elastomer blend is mainly determined by the elastic modulus at the application temperature and the glass transition temperature of the blend. The glass transition of the resins is higher than that of the elastomers, so the glass transition temperature of a resin–elastomer blend will increase by increasing the resin content [34] (Figure 2.17). The addition of resin decreases the elastic modulus of an elastomer, so the elastic modulus of a resin–elastomer blend will decrease by increasing the resin content. Figure 2.18 illustrates the increase in tan δ ($=E''/E'$, E': storage or elastic modulus, E'': loss or viscous modulus) (obtained from dynamic mechanical thermal analysis experiments)—for example, a decrease in the elastic modulus, E'—by increasing the aromatic hydrocarbon resin content in a polychloroprene–hydrocarbon resin blend [34] (see also *Fundamentals of Pressure Sensitivity,* Chapter 5, and *Applications of Pressure-Sensitive Products,* Chapter 7).

All resin–elastomer blends demonstrate a similar variation in tack as a function of the resin content (Figure 2.19) [34]. Little enhancement of tack is produced for resin contents lower than 50 phr (33 wt % resin). Between 50 and 80 phr resin contents (33 to 45 wt %) a sudden increase in tack is produced, and a rapid drop off in tack for resin contents above 80 phr is produced. Above 45 wt %, the aromatic hydrocarbon resin–polychloroprene system becomes overloaded in resin, incompatibility develops, and tack drops. Although the resin loadings may change depending on the elastomer and resin characteristics, the above trend is found in most resin-elastomer systems. The maximum tack in the resin–polychloroprene blend will be determined by the compatibility

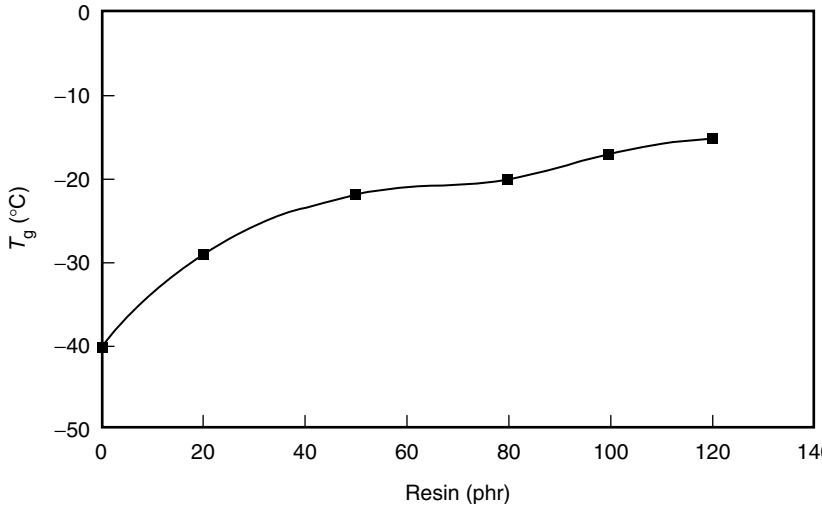


FIGURE 2.17 Evolution of the glass transition temperature of polychloroprene–aromatic hydrocarbon resin blends as a function of the resin content. T_g values were obtained from DSC experiments.

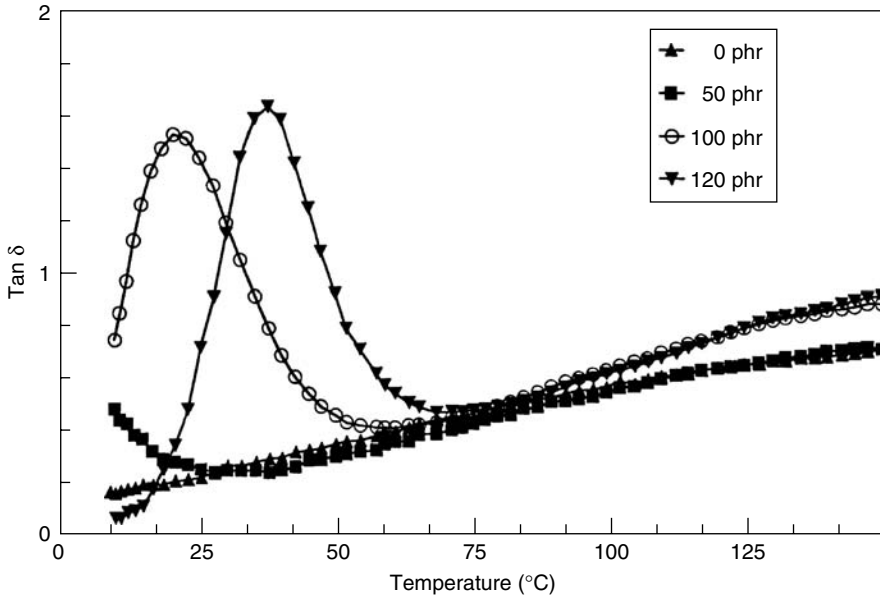


FIGURE 2.18 Variation in tan δ as a function of the temperature of polychloroprene–aromatic hydrocarbon resin blends containing different resin content. Frequency, 1 Hz. Target strain, 0.005. Dynamic mechanical thermal analysis (DMA) experiments.

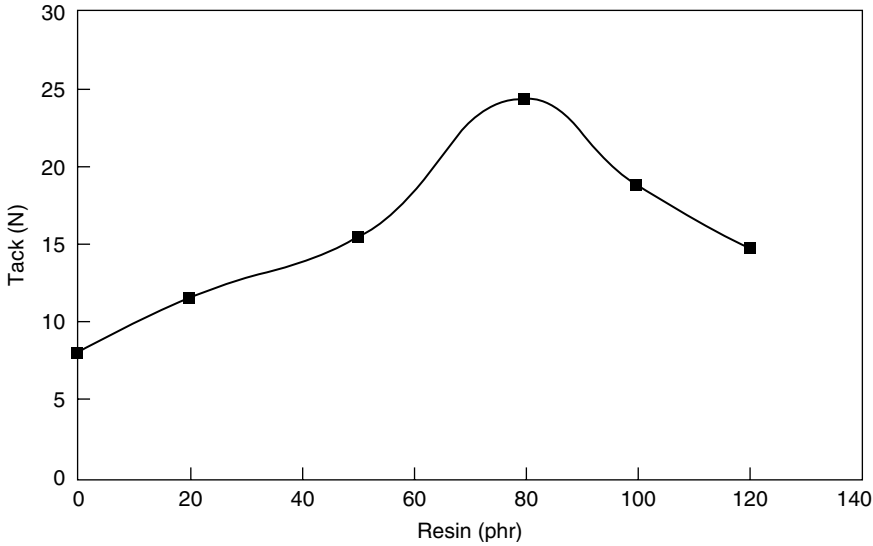


FIGURE 2.19 Evolution of the tack of polychloroprene–aromatic hydrocarbon resin blends as a function of the resin content. Tack was obtained as the immediate T-peel strength of joints produced with 0.6-mm-thick SBR strips placed in contact without the application of pressure. Peeling rate = 10 cm/min.

of the resin with the polychloroprene. Typically, the lower softening point of chemically similar resins will develop maximum tack at higher resin loadings than the higher softening point resins.

Adhesion (measured as peel resistance) of the resin-elastomer blends is generally enhanced for low resin loadings and decreases with increasing resin content [34]. Figure 2.20 illustrates the variation in T-peel strength of joints produced with polychloroprene–aromatic hydrocarbon resin blends, the same system for which tack is given in Figure 2.19. The maximun in adhesion corresponds to resin loading of 50 phr (33 wt %), decreasing suddenly for higher aromatic resin loading. A comparison of Figures 2.19 and 2.20 indicates that the beginning of tack development in polychloroprene–hydrocarbon resin blends corresponds to the decrease in adhesion.

The chemical nature of the tackifier also affects the compatibility of resin–elastomer blends. For polychloprene (a polar elastomer) higher tack is obtained with a polar resin (PF blend in Figure 2.21) than with a nonpolar resin (PA blend in Figure 2.21). Futher, the adhesion of resin–elastomer blends also decreases with increasing aromatic content in the resin [29]. Figure 2.22 illustrates a decrease in T-peel strength of roughened SBR/polychloroprene–hydrocarbon resin joints by increasing the MMAP cloud point. Because the higher the MMAP cloud point value, the lower the aromatic nature of the resin, the aliphatic aromatic resin–polychloroprene blends exhibit poor adhesion.

The addition of low-molecular-weight resins with narrow molecular weight distribution produces compatible resin–elastomer blends, whereas incompatible blends are obtained with resins with a wide molecular weight distribution. In a previous study [27],

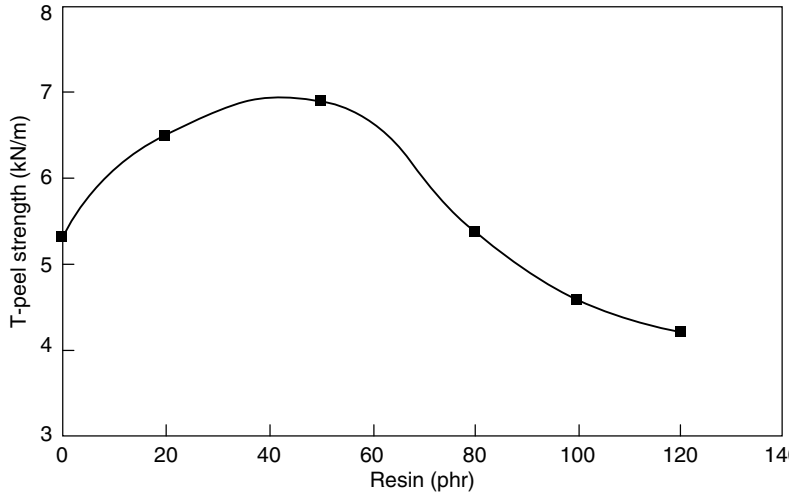


FIGURE 2.20 Evolution of the T-peel strength of SBR/polychloroprene–aromatic hydrocarbon resin/SBR joints as a function of the resin content. Peeling rate = 10 cm/min.

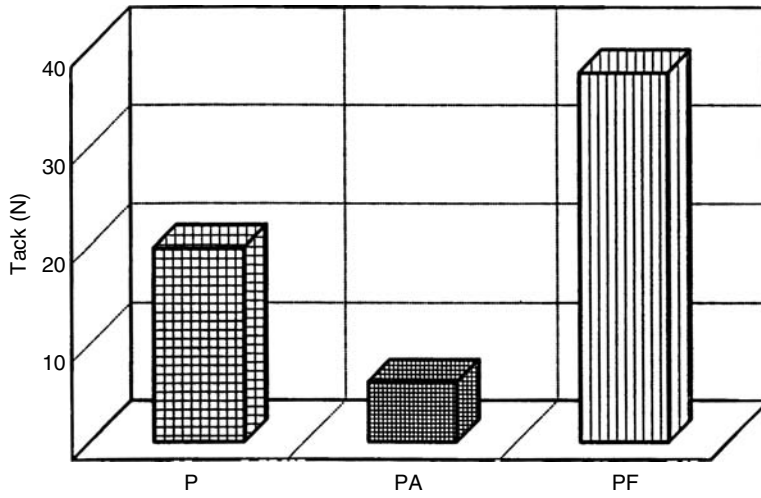


FIGURE 2.21 Tack of polychloroprene–hydrocarbon resin blends (33 wt % resin content) as a function of the nature of the hydrocarbon resin. Tack was obtained as the immediate T-peel strength of joints produced with 0.6-mm-thick SBR strips placed in contact without application of pressure. Peeling rate = 10 cm/min.

different aromatic hydrocarbon resins with different molecular weights and molecular weight distributions were added to a polychloroprene elastomer. Blends contain 17 wt % aromatic hydrocarbon resins. The polydispersity of one of the resins (*Piccolastic D125* from Hercules) was extremely high (M_w/M_n = 32.5). For the blend produced with this resin, a noticeable decrease in tack was found (PD blend in Figure 2.23)

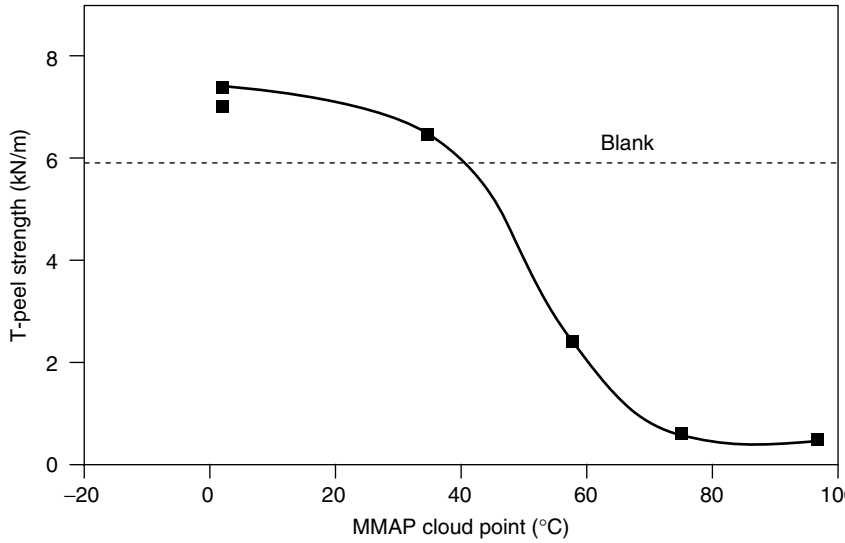


FIGURE 2.22 Evolution of the T-peel strength of SBR/polychloroprene–aromatic hydrocarbon resin/SBR joints as a function of the MMAP cloud point. Peeling rate = 10 cm/min.

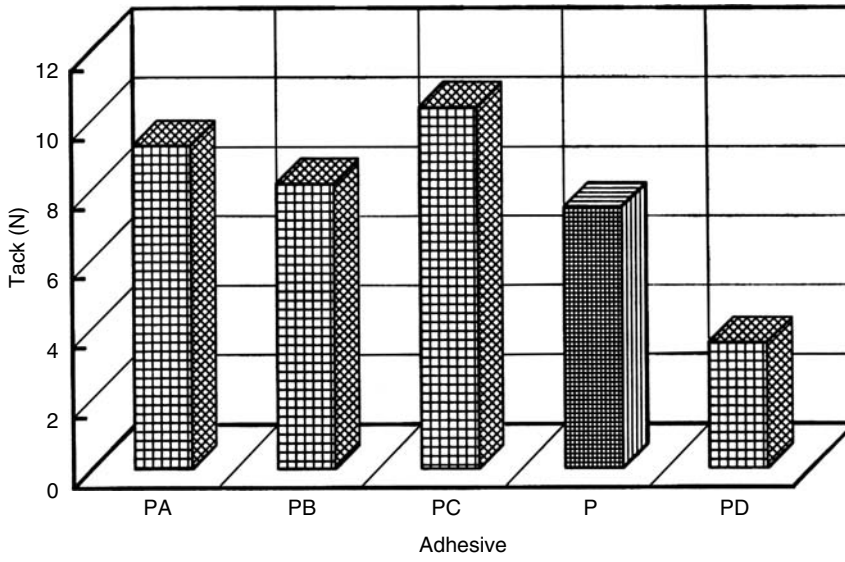


FIGURE 2.23 Tack of polychloroprene–aromatic hydrocarbon resin blends (17 wt % resin content) as a function of the molecular weight of the hydrocarbon resin. Tack was obtained as the immediate T-peel strength of joints produced with 0.6-mm-thick SBR strips placed in contact without application of pressure. Peeling rate = 10 cm/min.

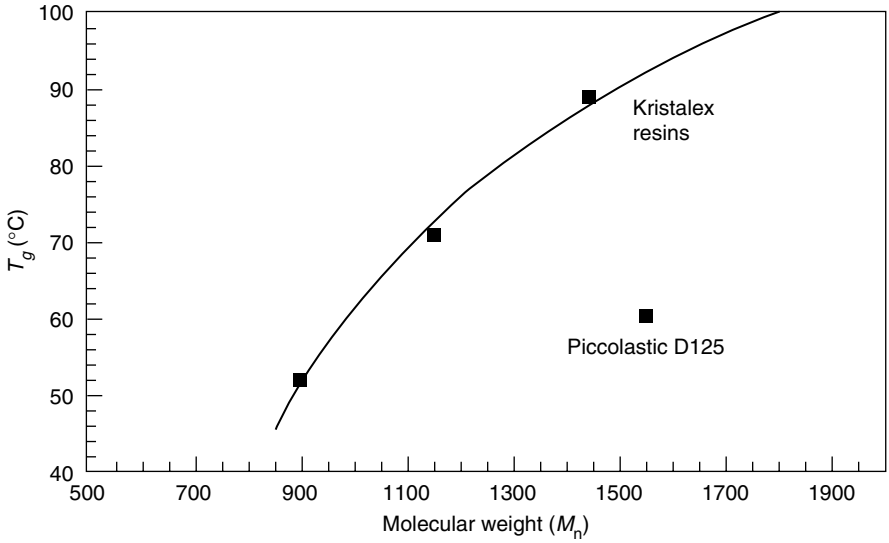


FIGURE 2.24 Evolution of the glass transition temperature of polychloroprene-aromatic hydrocarbon resin blends (17 wt % resin content) as a function of the average molecular weight in number of the hydrocarbon resin. T_g values were obtained from DSC experiments.

because incompatibility with the polychloroprene was produced. Incompatibility was evidenced using DSC (Figure 2.24), which demonstrates that the increase in the glass transition temperature in the *Piccolastic D125*-polychloroprene blend was much lower than for the blend produced with an aromatic hydrocarbon resin (*Kristalex 5140* from Hercules) with similar M_n value but smaller polydispersity ($M_w/M_n = 3.3$). Furthermore, the adhesion properties of the joint produced with the *Piccolastic D125*–polychloroprene blend were much lower than for the joints produced with blends containing resins with narrower molecular weight distribution (Figure 2.24). Whereas the tack of aromatic hydrocarbon resin–polychloroprene blends was not affected by the increasing molecular weight of the aromatic hydrocarbon resin (Figure 2.23), an increase in T-peel strength was obtained (Figure 2.25).

Mizumachi and coworkers [35–38] analyzed in great detail the miscibility in NR–tackifier blends. NR was blended in various ratios with several rosin and terpene tackifiers. The miscibility of the blends was assessed visually (transparency/opacity) as well as by optical microscopy. Miscibility was evidenced as phase diagrams. The miscible range of a blend system decreased as the molecular weight of a tackifier increased [35]. Furthermore, the esters of hydrogenated rosin and disproportionated rosin demonstrated comparatively good miscibility with NR, whereas polymerized rosin and its esters had poor compatibility with NR [36]. In another paper [37], the holding time was recorded as the required time for the PSA tape under shear load to completely slip away from the adherend. The holding time of miscible PSA systems tended to decrease as the tackifier content increased. This was ascribed to a decrease in plateau modulus of the PSA with increasing tackifier content. The holding time of immiscible PSA systems was

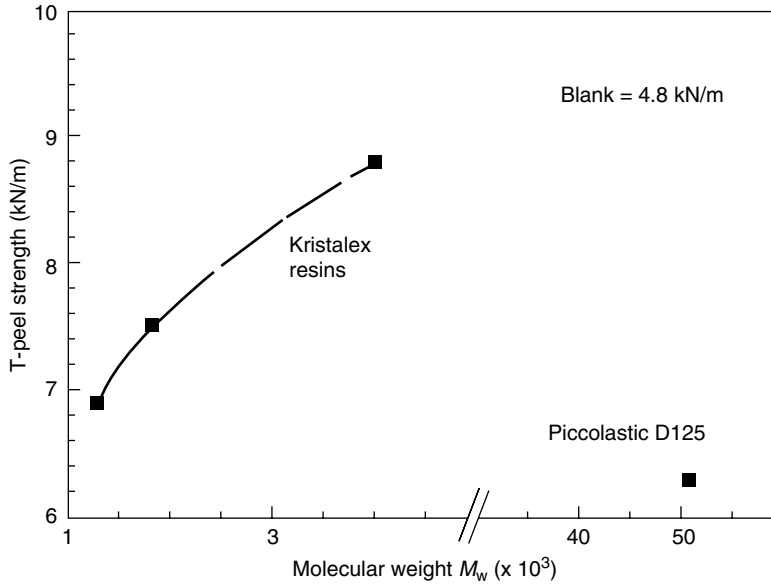


FIGURE 2.25 Evolution of the T-peel strength of roughened SBR/polychloroprene–aromatic hydrocarbon resin/SBR joints as a function of the average molecular weight in weight of the hydrocarbon resin. Peeling rate = 10 cm/min.

different from tackifier to tackifier due to differences in the extent of phase separation [37]. Peel strength (180°) of completely miscible NR–tackifier blends demonstrated the peak positions in the pulling rate–peel strength curves shifted to the lower velocity as the tackifier content increased [38]. On the contrary, completely immiscible PSAs had smaller peel strength than miscible ones and did not yield a manifest shift of peaks. In most adhesives, the fracture mode changed from cohesive failure to interfacial failure (between adhesive and adherend), slip–stick failure, and glassy failure (between the tape and adhesive) as the pulling rate increased [38].

Recently [39], acrylic tackifier was used as a tackifier for NR-based PSAs. They form two phases, but unlike traditional tackifiers, NR does not dissolve to any considerable extent in the acrylic (as predicted from the Wetzel theory). Furthermore, the behavior of the PSA can be adequately explained by its viscoelastic properties. For a good PSA, the ratio of storage modulus at high frequency to low frequency should be high (this also gives a higher loss tangent value at high frequency than at low frequency).

Viscosity, loop tack, and peel strength of epoxidized natural rubber-based PSAs was studied in the presence of 10–50 phr zinc oxide [40]. Coumarone–indene resin with loading from 20 to 100 phr was chosen as the tackifier resin, and toluene was used as solvent. The adhesive was coated on a paper substrate to give a coating thickness of 60 μm. Viscosity and loop tack of adhesive increased with increasing zinc oxide concentration. Peel strength increased with zinc oxide concentration up to 30–40 phr and dropped after the maximum value. This observation was associated with a different degree of

wettability of the adhesive on the substrate. However, for a fixed zinc oxide concentration, loop tack and peel strength exhibited a maximum value at 80 phr resin loading, after which both properties decreased with further addition of resin, an observation that was attributed to phase inversion. The optimum adhesion property was achieved in the PSA with 40 phr zinc oxide and 80 phr coumarone resin [40].

2.4.3 Plasticizers

Plasticizers are substances (usually low-molecular-weight diluents) that are incorporated into polymeric materials to improve their workability and increase flexibility. Polymeric plasticizers are low glass transition temperature (T_g) polymers that form homogeneous mixtures when blended with a polymer with higher T_g (see also Chapter 8).

Primary and secondary plasticizers can be distinguished. Primary plasticizers are compatible with the polymer, whereas secondary plasticizers are less compatible and are generally used in mixtures with primary plasticizers to confer an adequate balance of properties. About two thirds of plasticizers used today are diesters of phthalic anhydride with C_4–C_8 alcohols. The C_8 alcohols offer the best balance of properties for general-purpose plasticizers, with dioctyl phthalate being the most common. Other classes of plasticizers are triaryl phosphates, alkyl esters of dibasic alkyl acids, alkyl trimellitate esters, high-molecular-weight polyesters, and epoxies.

Plasticizers can be classified according to their chemical nature. The most important classes of plasticizers used in rubber adhesives are phthalates, polymeric plasticizers, and esters.

Phthalate plasticizers constitutes the biggest and most widely used plasticizers. The phthalate plasticizers are the most widely used. The linear alkyl phthalates impart improved low-temperature performance and have reduced volatility.

Most of the polymeric plasticizers are saturated polyesters obtained by the reaction of a diol with a dicarboxylic acid. The most common diols are propanediol, 1,3- and 1,4-butanediol, and 1,6-hexanediol. Adipic, phthalic, and sebacic acids are common carboxylic acids used in the manufacture of polymeric plasticizers. Some polyhydroxybutyrates are used in rubber adhesive formulations. Both the molecular weight and the chemical nature determine the performance of the polymeric plasticizers. Increasing the molecular weight reduces the volatility of the plasticizer but reduces the plasticizing efficiency and its performance at low temperature. Typical esters used as plasticizers are *n*-butyl acetate and cellulose acetobutyrate.

The mode of action of plasticizers can be explained using the gel theory [41]. According to this theory, the deformation resistance of amorphous polymers can be ascribed to the cross-links between active centers that are continuously formed and destroyed. The cross-links are constituted by microaggregates or crystallites of small size. When a plasticizer is added, its molecules also participate in the breaking down and reforming of these cross-links. As a consequence, a proportion of the active centers of the polymer are "solvated" and do not become available for polymer-to-polymer links; the polymer structure is correspondingly loosened.

The chemistry of plasticizers is related to the properties they impart to polymers. The following characteristics are decisive for their influence.

- *Molecular weight*. The increase in the molecular weight of the plasticizer decreases its volatility, migration, and softening efficiency.
- *Polarity*. The increase in the polarity of the plasticizer (e.g., existence of polar groups, substitution of aryl groups by alkyl ones) reduces softening efficiency, worsens low-temperature properties of the plasticized polymers, improves solvation, and reduces extractability by aliphatic solvents.
- *Alkyl chain*. The increase in the alkyl chain length and linearity improves the efficiency of the plasticizer and the low-temperature flexibility of the plasticized polymers.
- *Separation of ester groups*. Increasing the distance between ester groups increases solvation and softening efficiency.
- A_p/P_0 *ratio*. The A_p/P_0 ratio is calculated by dividing the numbers of carbon atoms in aliphatic chains in a plasticizer molecule by the number of ester groups present. The A_p/P_0 ratio correlates well with several properties of the plasticizers such as melting point, density, modulus, and water absorption.

Addition of a plasticizer decreases the T_g of the polymer and, in partially crystalline polymers, also influences both crystallization and melting. The amount of plasticizer affects its effectiveness. Thus, whereas the T_g of the polymer is strongly depressed by small plasticizer additions, the increase in the plasticizer content leads to lower decrease in T_g and in several systems two T_g values exist [42]. Therefore, the increase in the plasticizer content in polymers does not indicate a monotonic decrease in T_g.

Plasticizers reduce hardness, enhance tack, and reduce cost in rubber-based adhesives formulations. A plasticizer must be easily miscible and highly compatible with other ingredients in the formulations and with the surfaces to which the adhesive is applied. The compatibility and miscibility of plasticizers can be estimated from the solubility parameter values. Most plasticizers have Hildebrand solubility parameters ranging between 8.5 and 10.5. Their high miscibility and compatibility also lead to easier difussion of the plasticizer to the surface, decreasing the adhesion properties. Therefore, plasticizers should be carefully selected and combinations of two or more are often used.

It is desirable that the plasticizer compounded with a polymer be permanently retained. Loss of plasticizer changes the properties of a given formulation and can be produced by volatilization, extraction, or migration. The volatility of a plasticizer in a formulation can be related to the surface area, thickness of the polymeric material, and viscosity (e.g., molecular weight) of the plasticizer itself (see also *Applications of Pressure-Sensitive Products*, Chapter 8).

2.4.4 Fillers

Fillers may be broadly defined as solid particulates or fibrous materials, substantially inert chemically, incorporated in polymer compositions to modify properties or reduce

cost. Cost reduction is not the primary reason to incorporate fillers in adhesives, but they are used to impart specific properties such as flow, improved adhesion, mechanical, thermal, electrical, and optical properties, chemical and weather resistance, and rheologic behavior (see also Chapter 8).

There are a few excellent books dealing with the characteristics and properties of fillers. Two of the most interesting are *Handbook of Fillers and Reinforcements for Plastics* (Van Nostrand Reinhold, New York, 1978) and *Handbook of Fillers* (ChemTec Publishing, Toronto, Canada, 2000).

In adhesives, the correlation between tensile properties and adhesion is important. Fillers frequently increase hardness and reinforce adhesives, so the choice of filler and its concentration are often critical. In addition, adhesion may be affected by the filler's presence because of absorption of the coupling agents, change in the rheologic properties (reducing mechanical adhesion), or changing moisture permeability, which affects hydrolytic changes at the interphase. In some formulations, the addition of fillers also assists in the reduction of skrinkage during curing.

In rubber-based PSAs, fillers may affect properties such as cohesion, cold flow, rheology, and peel adhesion. Most fillers increase cohesion and reduce cold flow. In some formulations, even a small addition of filler dramatically reduces peel strength either because of interactions with the tackifier or because filler particles at the surface reduce the area of contact between the adhesive and the substrate.

Fillers are added to rubber-based adhesives for various purposes such as reduced cost, viscosity control, and resistance to weathering. In general, clay, calcium carbonate, and talc are the most common fillers added to rubber-based PSAs. Some rubbers are less demanding of fillers (e.g., BR, polybutadienes, etc.) than others.

The key properties of fillers used in rubber-based PSA formulations are as follows.

Density. Most fillers added to rubber-based formulation have a density between 2 and 2.7 g/cm^3, except barium sulfate (4–4.9 g/cm^3) and zinc oxide (5.6 g/cm^3). The addition of filler increases the free volume of the polymer and, in general, there is a critical concentration of filler at which the density of the formulation increases. The method of incorporation of filler in the adhesive formulation is important because air voids may appear when poor dispersion is produced.

Particle Shape and Roughness. The shape of filler particles is determined by their crystal structure and cleavage. The surface area of the particles increases by milling, but it retains the original feature. The interactions between the filler surface and the polymer depend on the crystal structure (which dictates the chemical organization) and on the functional groups (which may react with the polymer). In synthetic fillers, the surface organization also depends on the internal structure of the particles. The surface roughness is determined by the shape of the filler particles and is important in the development of adhesion forces between the filler and the polymer. Platelet particles (i.e., clay) usually interact better with polymers than spherical particles do.

Particle Size. In general, fillers used in rubber-based PSAformulations should have a particle size smaller than 5 μm to avoid settlement from solutions. Fumed and precipitated silicas and ultrafine titanium dioxide particles are produced in primary particle sizes smaller than 10 nm. Most of the mineral fillers in the smallest particle sizes have a size greater than 100 nm. Synthetic fillers with a particle size of a few

nanometers usually tend to aggregate and agglomerate in their powder forms. Thus, for the dispersion of fillers, agglomerate and aggregate size is usually as relevant as primary particle size. The lower the primary particle size of the filler, the higher the tendency to agglomerate. The small particle size filler is difficult to disperse (although it provides more transparency and better reinforcement). Fillers with particle size of about 0.1 μm demonstrate an adequate balance between performance and dispersion in adhesive formulations [43].

Particle Size Distribution. Although almost all fillers are fractioned to remove the coarser particles, a distribution of particles is generally found. The particle size distribution may affect the viscosity, rheologic properties, and the amount of filler to be incorporated in a formulation. In general, narrow particle size distributions are recommended in fillers to obtain the best performance in rheologic, mechanical, and optical properties.

Specific Surface Area. Surface area is one of the most important properties of fillers. The specific surface area comprises the total surface of the particles, including the pores and at least part of the free volume of the aggregates. Larger, nonporous particles such as talc have the lowest specific surface areas. Fillers with small particle size that are not very porous, such as calcium carbonate and clay, occupy the middle range of specific surface area. Very small particles (precipitated silicas), formation of aggregates (fumed silica, furnace carbon blacks), and minerals with high porosity (sepiolite, attapulgite) yield fillers with the highest surface areas. Specific surface area is related to particle size in nonporous or poorly porous fillers. Further, the specific surface area depends on the filler treatment. Fillers with moderate surface areas are recommended in adhesive formulations [44].

Degree of Agglomeration. Some fillers, such as clay, carbon blacks, and fumed silicas, have a natural tendency to agglomerate. Van der Waals forces are primarily responsible for the agglomeration of fillers during production and storage. However, agglomeration of filler particles is complex because it can be also influenced by the particle size, chemical groups on the filler surface, moisture level, and the method of filler production. For instance, interactions between silanol groups on the filler surface are responsible for the agglomeration of fumed silicas. The degree of agglomeration of fillers affects the dispersion and the rheologic properties of adhesives [45], and disagglomeration of fillers during adhesive manufacturing should be produced to obtain acceptable properties.

Aspect Ratio. Aspect ratio is the length of the particle divided by its diameter. A high aspect ratio (typically provide by fibers) provides reinforcement of polymers. The majority of fillers have a low aspect ratio (below 10).

Surface Energy. The surface energy of a filler determines its wettability and adhesion properties. The dispersive nonpolar component of the surface energy of a filler can be associated with polymer–filler interactions, whereas the polar component of the surface energy is associated with filler networking and agglomeration. Calcium carbonates, zinc oxide, and most carbon blacks have dispersive components of about 50 mJ/m^2, whereas titanium dioxide and fumed silica have dispersive components of 80 mJ/m^2 [46]. Talc has the highest dispersive component (130 mJ/m^2) [46].

Moisture Content. The presence of water in the filler is not usually beneficial. Most fillers added to adhesives have a moisture content that is lower than 1 wt %. Only

precipitated silicas and sepiolite contain about 5–10 wt % moisture. For some applications, fillers must be completely dried to exhibit adequate performance. Moisture absorbed on the surface of fillers impacts the rate and extent of curing of rubber-based adhesives.

Hydrophilic/Hydrophobic Properties. Grafting and surface coating are two procedures commonly used to impart hydrophilic properties to fillers. Grafting with silanes and titanates provides improved filler compatibility. Surface coating with polyethylene glycol is also effective to increase the hydrophilic surface of fillers. For kaolin, surface coating with fatty acids (stearic acid, oleic acid) and derivatives (magnesium stearate, calcium stearate) also imparts hydrophilic properties.

However, the hydrophilic surface of fillers is often a disadvantage because the majority of polymers are hydrophobic. Hydrophobic properties are also important to avoid the agglomeration of particles during storage. Surfactants (tetrabutylammonium chloride, sodium dodecyl sulfate) and fatty acid derivatives give improved hydrophobic properties to calcium carbonate [47].

The most common fillers used in rubber-based PSA formulations will be briefly described. On the basis of their chemical structure, these fillers may be classified into four broad groups: silicates, silicas, calcium carbonate, and carbon blacks.

Silicates. Clay and talc are the most common fillers in rubber-based PSA adhesive formulations. Both have a platy shape that favors the interactions with elastomers.

Clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Kaolin clay, China clay, bentonite, Fuller's earth, and vermiculite are clay minerals that are used as fillers. Kaolin is the most common clay used as a filler in rubber-based adhesives. Kaolin is a product of hydrothermal decomposition under acid conditions of granite and white feldespate. It is characterized by a density of 2.6 g/cm^3; pH of water suspension 3.5–11; particle size 0.2–7 μm; oil absorption 45–120 g/100 g; and specific surface area 8–65 m^2/g. The mined clay mineral must be refined to impart good properties as a filler and the grinding process is used to reduce size and delaminate the stacks of the mineral. Further, the calcination of kaolin above 450°C alters the clay structure and improves electrical resistance and brightness.

Talc ($Mg_3Si_4O_{10}(OH)_2$). Talc is the major constituent of soapstone rocks and has a plate-like structure with a relatively important aspect ratio. It is characterized by a density of 2.7–2.85 g/cm^3; pH of water suspension 8.7–10.6; particle size 1.4–19 μm; particle thickness 0.2–6 μm; aspect ratio 5–20; oil absorption 22–57 g/100 g; and specific surface area 2.6–35 m^2/g.

The composition of talc varies depending on its source and tremolite content. Talc processing is performed using dry and wet processes. The dry process consists of selective mining (mainly by color and mineralogy), followed by grinding. The finest grades (3–10 μm) are obtained by micronization of ground particles in jet mills. The wet process separates contamination by flotation, so more pure talc materials are obtained. After flotation, the talc is filtered, dried, and milled by impact mills or jet mill micronization. Some grades of wet processed talcs have a silane surface treatment.

The layers in the plate-like structure of talc are joined by very weak van der Waals forces, and therefore delamination at low shear stress is produced. The plate-like structure provides high resistivity and low gas permeability to talc-filled polymers. Furthermore, talc has several other structure-related unique properties: low abrasiveness, a

lubricating effect, and hydrophobic character. Hydrophobicity can be increased by surface coating with zinc stearate.

Silicas. Although natural quartz, cristobalite, and opal are used as fillers, only synthetic products (fumed and precipitated silicas) find use as fillers in rubber-based PSA adhesives.

Fumed Silica (SiO_2). Fumed silicas are common fillers in NR- and SBR-based adhesives. Fumed silica are widely used as fillers in several polymeric systems, to which it confers thixotropy, sag resistance, particle suspension, reinforcement, gloss reduction, and flow enhancement.

Fumed silica is obtained by the gas reaction between sand and dry HCl to yield silica tetrachloride ($SiCl_4$) vapor. $SiCl_4$ is mixed with hydrogen and air in a burner (1800°C), where fumed silica is formed.

$$SiCl_4 + 2H_2 + O_2 \rightarrow SiO_2 + 4HCl \tag{2.1}$$

The primary particles of fumed silica leaving the burner are in a molten state; therefore, upon collision they are able to coalesce, forming bigger particles (aggregates). During cooling and collection, these aggregates produce agglomerates. These agglomerates can be disintegrated upon mixing during the adhesive manufacturing process. Some typical properties of fumed silicas include a density of 2.0–2.2 g/cm^3; pH of water suspension 3.6–4.5; primary particle size 5–40 nm; aggregate size 0.2–15 μm; density of silanol groups 1.5–4.5 groups/nm^2; oil absorption 100–330 g/100 g; and specific surface area 50–400 m^2/g.

Fumed silicas are characterized by several interesting properties, which makes them suitable additives to adhesives, such as the following.

- Fumed silicas have an amorphous nature that is probably caused by fast cooling during the manufacturing process. It is an important benefit because it does not cause silicosis.
- The surface of fumed silica is highly hydrophilic. Several kinds of silanol groups are produced during manufacturing (about 3–4.5 OH groups per nm^2), which are essential to impart rheologic properties. The mechanism of thickening liquids by fumed silica is explained by hydrogen bond formation between neighboring aggregates of silica, leading to the formation of a regular network [48]. Upon application of shear some of these bonds are broken, which reduces viscosity. The initial stage is regained when the material is left to stand. For some applications, the hydrophobic properties of fumed silicas are important. Through treatment with the appropriate silanes, the concentration of silanol groups can be reduced up to about 1.5 OH groups per square nanometer.
- The morphology of fumed silica is spherical and is composed of grain-like agglomerates. The mixing process of fumed silica should produce the formation of small aggregates, which form network of chains interconnected throughout the polymer–filler mixture. Overmixing reduces the size of the aggregates too much and only a partial network is created.

Precipitated Silicas (SiO_2). Precipitated silicas are common fillers used to impart thixotropy to NR- and SBR-based formulations. Precipitated silica is produced by the reaction

of sodium silicate ($3SiO_2 \cdot Na_2O$) with sulfuric or hydrochloric acid. The concentration of reactants, rates of addition, temperature, and drying are process variables determining the properties of the precipitated silica, such as oil absorption, specific surface area, porosity, primary particle, and agglomerate size and shape. The moisture content in precipitated silicas is high (3–7%) and three types of water are available: free water (easily removed by heating at 105°C), adsorbed water (removed by heating at 200°C), and constitutional water (removed at 700–900°C).

Some typical properties of precipitated silicas include a density of 1.9–2.1 g/cm^3; pH of water suspension 3.5–9; primary particle size 5–100 nm; aggregate size 1–40 μm; density of silanol groups 5–12 groups/nm^2; oil absorption 60–320 g/100 g; and specific surface area 12–800 m^2/g.

The thickening mechanism of precipitated silicas is similar to that of fumed silicas. Precipitated silicas have more silanol groups than fumed silicas, but they have a lower concentration of silica (precipitated silicas generally contain some sodium sulfate).

Calcium Carbonate ($CaCO_3$). Calcium carbonate is often used as a filler in PSA formulations. As a filler, calcium carbonate allows cost reduction and improved mechanical properties. Calcium carbonate is found in sedimentary rocks (chalk, limestone), marbles, and minerals (dolomite). Some typical properties include a density of 2.7–2.9 g/cm^3; pH of water suspension 9; particle size 0.2–30 μm; oil absorption 13–21 g/100 g; and specific surface area 5–24 m^2/g. Depending on their origin and history of formation, as well as their impurities, calcium carbonates have different properties. Three major technological processes are used in the production of calcium carbonate filler: milling, precipitation, and coating. However, the most common calcium carbonate filler is processed by milling using a dry or wet method [49]. Dry milling provides ultrafine calcium carbonate grades (particle size of about 0.6 μm). Natural milled calcium carbonates are added to decrease the cost in rubber-based adhesives.

Carbon Blacks. Carbon blacks are typical fillers for reinforcing rubber but they are not commonly incorporated in PSA formulations. Carbon blacks are synthetic materials that essentially contain carbon as the main element. The structure of carbon black is similar to that of graphite (hexagonal rings of carbon forming large sheets), but its structure is tridimensional and less ordered. The layers of carbon blacks are parallel to each other but not arranged in order, usually forming concentric inner layers (turbostratic structure). Some typical properties are a density of 1.7–1.9 g/cm^3; pH of water suspension 2–8; primary particle size 14–250 nm; oil absorption 50–300 g/100g; and specific surface area 7–560 m^2/g.

Carbon blacks are obtained by pyrolysis or combustion of hydrocarbon-containing materials (hydrocarbon gases, viscous residual aromatic hydrocarbons). Thermal and furnace carbon blacks are used in rubber-based PSAs. In the thermal decomposition process, natural gas is fed, in the absence of air, into a generator at a temperature of 1300°C, where it undergoes cracking. The thermal carbon blacks are obtained from the stream of product gases. The oil-furnace process is the most prevalent method of carbon black production. A reactor is fed by liquid hydrocarbon feedstock, which is mixed with preheated air and natural gas. The furnace carbon back is obtained from the combustion gases. In general, furnace carbon blacks have lower particle size and higher specific surface area than thermal carbon blacks.

Particle and aggregate size are the most important factors in carbon blacks. During the manufacture of carbon blacks, primary particles are obtained in gas or liquid states. As primary particles are formed at high temperature, they tend to adhere to each other and partial fusion occurs, producing aggregates. The aggregates can also be joined to produce agglomerates. The aggregates determine the properties of the carbon blacks because they cannot break, even under very abrasive processing methods. On the other hand, depending on the manufacturing process, different active groups are exposed to the surface of carbon black; these groups affect wetting, dispersion, adsorption of moisture, and reinforcing of polymers by carbon blacks.

2.4.5 Curing Agents

Raw rubber is an entanglement of high-molecular-weight hydrocarbon chains. Consequently, rubber flows upon standing and does not retain its shape. For rubber to become useful, its chains must be permanently linked together to increase its strength. Rubber can be cross-linked (i.e., vulcanized) by heating with sulfur. During vulcanization, sulfur linkages form bridges between rubber chains.

The vulcanization process takes hours or even days to be produced. Accelerators can be added to reduce the vulcanization time. Zinc oxide is an activator of the accelerator system, and the amount generally added in rubber formulations is 3 to 5 phr. Fatty acids (mainly stearic acid) are also added to avoid low curing rates. Today, the cross-linking of any unsaturated rubber can be accomplished in minutes by heating rubber with sulfur, zinc oxide, a fatty acid, and the appropriate accelerator.

Vulcanization changes the physical properties of rubbers. It increases viscosity, hardness, modulus, tensile strength, and abrasion resistance and decreases elongation at break, compression set, and solubility in solvents. All these changes are proportional to the degree of cross-linking (number of cross-links) in the rubber network, with the exception of tensile strength. On the other hand, rubbers differ in their ease of vulcanization. Because cross-links form next to double carbon–carbon bonds, the highly unsaturated rubbers are the most easily cured (for instance, NR is more easily vulcanized than SBR).

Rubber-based adhesives can be used without cross-linking. When necessary, essentially all the cross-linking agents normally used in the vulcanization of NR can be used to cross-link elastomers with internal double carbon–carbon bonds. A common system, which requires heat to work, is the combination of sulfur with accelerators (zinc stearate, mercaptobenzothiazole). The use of a sulfur-based cross-linking system with zinc dibutyldithiocarbamate or zinc mercaptobenzothiazole allows curing at room temperature. Common curing agents used for rubber-based PSAs are discussed in Chapter 8.

The influence of the gel content on creep resistance and peel behavior in polyisoprene–tackifier blends was studied in Ref. [50]. The gel content was achieved by cross-linking the adhesives with electron beam irradiation. The molecular weight of the soluble fraction in the blend was always dominated by that of the initial elastomer. Creep resistance was achieved either through molecular weight increase or gel content increase. However, the peel resistance is strongly influenced by the initial elastomer molecular weight

and further cross-linking did not provide performance equivalent to that obtained from high-molecular-weight materials.

2.4.6 Antioxidants

In rubber-based adhesives it becomes necessary to prevent their properties from changing during their service life. Oxidative changes induced by thermal and ozone exposition and UV light can dramatically affect the service life of rubber-based adhesives (see also Chapter 8 and *Applications of Pressure-Sensitive Products*, Chapter 7). More precisely, the rubber and resin are quite susceptible to oxidative degradation. Environmental and physical factors exert detrimental effects on rubber-based PSA performance. These effects can be mitigated by the incorporation of low levels of stabilizers during the fabrication process of the adhesives.

Antioxidants and stabilizers occupy a key position in the performance of adhesives. The terms "antioxidants" and "stabilizers" are generally used to describe chemical agents that inhibit degradative effects of oxygen, light, heat, and high temperature. Rubber technologists also use the terms "antidegradants," "antifatigue agents," "inhibitors," and "antiozonants." It is more convenient to use the term antioxidant to comprehensively describe "all chemical agents that act to inhibit oxidation of a polymer matrix arising from the adverse effects of mechanical, thermal, photochemical, and environmental factors during the manufacture of the polymeric material and throughout the service life of the end-use product."

Most rubbers used in adhesives are not resistant to oxidation. Because of the degree of unsaturation present in the polymer backbone of NR and SBR, they can easily react with oxygen. BR, however, possesses a small degree of unsaturation and is quite resistant to oxidation. The effects of oxidation in rubber-based adhesives after some years of service life can be assessed using FTIR spectroscopy. The ratio of the intensities of the absorption bands at 1740 cm^{-1} (carbonyl group) and 2900 cm^{-1} (carbon–hydrogen bonds) significantly increases when the elastomer has been oxidized.

Oxygen attacks rubber because of the presence of two unpaired electrons, which may act as two free radical species able to react with the unsaturation in hydrocarbon molecules. The radical species formed are highly reactive and very unstable, so they will be rapidly converted to more stable products. For most rubbers and resins, these radicals combine to form cross-links that cause hardening and color darkening. In NR, the cross-linking of these radicals is hindered because of the bulkiness of the methyl side group. Consequently, these radicals prefer to disproportionate and cleave. This reduces the molecular weight and NR softens upon aging.

The oxidation of rubbers and resins can be slowed considerably and the service lifetime extended through the addition of antioxidants. Antioxidants scavenge the propagating radicals before they have a chance to react with the polymer chains. Phenols (hindered phenols, hindered bisphenols, hindered thiobisphenols, polyhydroxy phenols) are the most effective antioxidants for rubber-based PSAs.

Another method for slowing the oxidation of rubber adhesives is to add a compound that destroys the radicals. These materials are called hydroperoxide decomposers, preventive antioxidants, or secondary antioxidants. Phosphites (phosphite esters,

organophosphite chelators, dibasic lead phosphite) and sulfides (i.e., thiopropionate esters, metal dithiolates) are typical secondary antioxidants.

Antioxidant activity is not a linear function of concentration. As the antioxidant level increases, less and less improvement in oxidative stability is noted. Therefore, just enough antioxidant should be added to rubber adhesives, typically 1 to 2 phr.

When two antioxidants are used together, a synergistic improvement in activity usually results. Synergism can arise from three combinations:

- Two chemically similar antioxidants (for instance, two hindered phenols): Homosynergism
- Two different antioxidants functions that are present in the same molecule: Autosynergism
- The cooperative effect between mechanistically different classes of antioxidants, such as the combined effect of primary and secondary antioxidants: Heterosynergism

UV Absorbers. The UV component of sunlight (wavelength 280–400 nm) can cause degradation of polymers, mainly UV radiation with a wavelength between 310 and 330 nm. Therefore, UV absorbers or light stabilizers are also important components in extending the service life of rubber-based PSAs. UV absorbers act by absorbing UV light, hence retarding the photolysis of hydroperoxides. The light stabilizers most commonly used in rubber-based PSAs are organic UV absorbers. These stabilizers operate by absorbing the damaging UV radiation and re-emitting the energy at a longer wavelength as infrared radiation (i.e., heat), which is harmless to the polymers. The most common organic UV absorbers are modified benzophenones and benzotriazole derivatives. 2-Hydroxybenzophenones and 2-hydroxybenzotriazoles are the most typical organic UV absorbers. Both are relatively stable to light between 300 and 360 nm and have high molar absorption in this region. In most cases, the degree of UV protection afforded increases with the additive's concentration. The protective effect also depends on the thickness of the rubber material (it is less marked in thin films).

2.4.7 Solvents

The solvent plays an important role in the performance of rubber-based PSAs. The solvent is the carrier for all components of the adhesive. Furthermore, the solvent controls the viscosity, open time, tack, and adhesion of rubber-based adhesives.

A particular case in which the solvent is important is in contact adhesives, which for some time after application have enough cohesive strength and knitting ability that two surfaces coated with the adhesive have green strength immediately after they are mated. *Knitting ability* is an autoadhesion phenomenon in which the elastomer molecules are mobile enough to quickly form a bond immediately after contact with little or no applied pressure. Few elastomers have this ability; polychloroprene is one of them. *Green strength* indicates that the adhesive bond is strong enough to be handled a short time after the adherends are mated but much before full cure is obtained. The choice of solvent in contact adhesives is critical because the solvents are chosen in such a way that a rapid

evaporating solvent is used as carrier medium and a slower evaporating solvent provides tack during bonding.

2.5 Most Significant Rubber-Based PSAs

The most significant rubber-based PSAs include NR-based formulations, BR- and PIB-based adhesives, and SBR-based adhesives.

2.5.1 Natural Rubber-Based PSAs

Most often, NR adhesives can be precoated onto fabric, paper,or film to provide pressure-sensitive tapes. NR-based adhesives can be divided in two types, wet bonding and dry bonding. *Wet bonding* adhesives are applied on substrates in a fluid state, and the bond is formed by drying. The *dry bonding* NR adhesives are pressure sensitive, and their bonding does not need a supplemental liquid medium because it is allowed by their special viscoelasticity.

Adhesives made from the various forms of NR exhibit similar characteristics, although some properties are altered by the addition of curatives. These characteristics include the following:

1. Excellent tack.
2. Very good water and moisture resistance.
3. High flexibility.
4. *Brittleness with age.* Degradative oxidation can be produced, even after vulcanization, due to oxygen and ozone attack to the double carbon–carbon bonds. Adequate antioxidants must be added if aging is a key factor in performance.
5. *Poor resistance to organic solvents and oils.* It can be partially reduced in vulcanized systems.
6. Low to moderate cost.
7. *A wide range of substrates can be bonded.* The inherent tackiness of NR enables it to coat most nonpolar substrates (mainly plastics and rubbers).
8. Good electrical and thermal insulators.

The coating of NR-based formulations requires the effective mixing of tackifiers, plasticizers and polymer. NR adhesives accept a wide variety of compounding ingredients.

1. *Thickeners* can be added to increase the viscosity of the NR adhesives. Natural materials such as casein or karaya gum can be used as thickeners, but synthetic polymers are also used (methyl cellulose and derivatives, polyacrylates).
2. Hydrocarbon *resins*, rosin, rosin ester, coumarone–indene resins, and terpene resins can be directly added.
3. *Reinforcing agents* can be added to increase the cohesive strength of NR adhesives;
4. *Plasticizers* and oils, curatives, and accelerators may also be added.
5. *Softeners* (e.g., liquid polybutenes and lanolin) can be added.

Specific formulations of NR adhesives can be found in Refs [51] and [52].

NR adhesives perform adequately under peeling stresses. The peel strength can vary from a few N/m (Newton/meter) in PSA formulations to "substrate tear" in vulcanized compounds used in hose, belting, and tire products.

Nonvulcanizing NR adhesives typically withstand temperature ranges between –30 and 65°C. Vulcanized NR adhesives can perform between –40 and 150°C.

NR PSAs with high tackifier content can be used as commercial tapes and surgical plasters. These PSAs require the elimination of the gel fraction and a reduction in molecular weight to facilitate solution. Rubber-based solution PSAs are recommended for labels, protective films, and tapes (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Latex compounds have been typically used in paper, textiles, and construction. One of the most popular applications is self-sealing envelopes. This application is based on the fact that when NR dries, some soluble nonrubber compounds migrate to the surface by water transport, leaving a thin film when drying is completed. This film reduces the surface tack on the rubber and, when pressed against a similar film, the nonrubber layer is displaced, allowing the two rubber surfaces to create a bond. Zinc diethyldithiocarbamate is added to prevent fungi and bacteria degradation. In some cases small amounts of a plasticizer (polybutene) or an adhesion promoter (polyvinyl acetate latex) can be added. Printable PSA sheets and removable PSA formulations can be manufactured with thickened, pigmented, and tackified NR latex.

Vulcanizing latex adhesives are used in the manufacturing of textiles, rugs, and carpets. The vulcanizing ingredients are sulfur, zinc oxide, and accelerators (for example, zinc dibutyldithiocarbamate and zinc mercaptobenzothiazole to produce vulcanization at room temperature).

2.5.2 Butyl Rubber and PIB-Based Adhesives

All grades of regular BR are tacky and rubbery and contain less unsaturation than NR or SBR. On the other hand, low-molecular-weight grades of PIB are permanently tacky and are clear white semiliquids, so they can be used as permanent tackifiers for PSAs. Low-molecular-weight PIBs also provide softness and flexibility and act as adhesion promoters for difficult-to-adhere surfaces (e.g., polyolefins).

The cohesive strength of these adhesives can be modified by blending BR and PIB. Higher strength is obtained by using high-molecular-weight PIB or BR. Blends of BR or PIB with chlorinated BR demonstrate improved cure properties.

The extremely diverse nature of the isobutene family of polymers makes difficult to make general statements, although the following characteristic properties can be listed:

1. *Superior water and moisture resistance.* Butyl is by far the best elastomer to provide resistance to water and moisture.
2. *High initial tack.* The adequate choice of butyl or PIB provides excellent building tack (ability to produce quick adhesion by applying low pressure).
3. *Low air and gas permeability.* The amorphous and highly saturated nature of the polymer chain prevents permeation of air and gases.

4. *Good resistance to oils.* Mainly PIB polymers resist high-oil-content materials. In some cases, swelling may occur.
5. *Good flexibility and impact resistance.* This is due to the amorphous nature of the polymers.
6. *Excellent aging.* This is due to the high degree of saturation in the polymer chain;
7. *Heat resistance.* It depends on the content of PIB in the BR polymer: The higher the PIB content, the lower the heat resistance and the higher the tack.
8. *Relatively low strength.* Even when cured or cross-linked, BR tends to creep under load.
9. *Wide substrate range.* BR and PIB stick to most surfaces, including polyolefins.

BR is similar to NR in its ability to compound with other materials. Some specific aspects related to additives for BR are given below.

1. *Pigments and fillers.* In general, BR and PIB polymers are compatible with a wide range of fillers. The same fillers and pigments can be added to BR and PIB. Very fine pigments (clays, precipitated silicas, thermal and furnace carbon blacks) increase cohesive strength and stiffness and reduce tack, whereas coarser pigments (aluminum hydrate, whiting) increase tack with a moderate increase in cohesive strength. Zinc oxide increases tack and cohesive strength and influences the vulcanization of BR. Calcium carbonate can also be added to decrease cost without a detrimental effect on mechanical properties.
2. *Tackifiers.* Resins are generally added to adjust the desired tack. In general, resins must be used with plasticizers to obtain a good balance between tack and cohesive strength. Typical tackifiers are polyterpenes, although hydrocarbon resins and modified rosins and rosin esters can also be used. In some cases, terpene–phenolics or phenol–formaldehyde resins are added to increase adhesion.
3. *Plasticizers.* Polybutene is the most common, although paraffinic oils and certain phthalates (i.e., ditridecyl phthalate) can also be added in the formulations.
4. *Antioxidants.* Antioxidants are rarely needed because of the highly saturated nature of the polymer chains. If protection against severe environmental aging conditions is needed, typical antioxidants can be added. In some cases, zinc dibutyldithiocarbamate (0.05–0.2 wt %) or butylated hydroxytoluene can be used as stabilizers.
5. *Adhesion promoter.* Epoxy silane can be added to increase adhesion to glass (mainly for BR sealants).

Specific formulations of BR and PIB adhesives can be found in Chapter 10 of the *Handbook of Adhesives*, 3rd edition (Van Nostrand Reinhold, New York, 1990).

Pressure-sensitive precoated films are supplied in forms quite similar to those of NR. BR and PIB are used for the adhesion of several substrates including nonporous and difficult-to-adhere materials (e.g., polyolefins). Other common substrates are PVC, polyester film, and paper.

The BR and PIB adhesives have permanent tack but relatively low cohesive strength. Cohesive strength is provided by adding NR, fillers, or tackifiers. Furthermore, these adhesives have excellent resistance to chemicals, oils, and aging.

New copolymers based on a copolymerization of isobutylene and *p*-methylstyrene with improved heat resistance have been reported [53]. Once copolymerization was accomplished, the polymer was selectively brominated in the *p*-methyl position to yield a terpolymer called EXXPO. In contrast to butyl and halobutyl, the new terpolymer has no unsaturation in the backbone and therefore demonstrates enhanced thermal stability and resistance to oxidation. The hydrocarbon nature of the new terpolymer results in excellent compatibility with hydrocarbon resins and oils.

Generally, blends of BR with different molecular weights are used. It has been shown [54] that the peel forces of PIB-based PSAs are only qualitatively described by linear viscoelasticity. BR adhesives are used as preformed tapes and hot-melt PSAs.

Tapes and Labels. Formulations mainly include blends of BR and tackifier. Permanent tack can be provided using low-molecular-weight PIBs and find application as label PSAs. The cohesive strength of BR adhesives is low compared to that of NR and can be increased by the addition of NR or particular resins and fillers. The polymer formulation is precoated onto a suitable carrier (film, reinforcement). General-purpose tapes, surgical tapes, electrical tapes, and pipe wrap tapes can be included in this group. The resistance of BR and PIB to aging and permanent tack also made the materials adequate for removable PSA labels and freezer label adhesives.

Preformed sealing tapes are widely used in construction applications and for glazing applications in automotive glass. Tapes for corrosion protection of steel pipes contain BR, cross-linked BR, regenerated rubber, tackifier, filler, and antioxidants. Such adhesives are coated on a nonwoven carrier. Air seal tape is also made with BR.

Hot-melt PSAs require heating to melt and subsequent cool-down. BR and PIB provide flexibility at low temperature, and impart improved chemical resistance and enhanced aging. Hot-melt formulations include BR, petrolatum and amorphous polypropylene, and hydrocarbon oils, polybutenes, and microcrystalline waxes (to reduce viscosity). The most common applications include carton closing and appliances manufacture.

Sealants for insulated glass window are based on butyl polymers. These sealants have excellent weathering and aging and low-moisture vapor transmission and are nonfogging.

Self-curing butyl adhesives can be used for laminating PE film and for flocking adhesives. One of the most important applications is the use of BR as curing, solvent dispersed, and contact grade for roofs manufacturing on industrial buildings.

Precoated butyl latex compounds onto fabric can be used for PSAs in foil and paper lamination. These PSAs are also used in packaging and for bonding polyolefins (they require adequate formulation).

2.5.3 Styrene–Butadiene Rubber-Based Adhesives

SBR adhesives are used in applications where low stress but high flexibility and resistance to shock are needed. If aging is critical, SBR adhesives should not be used. SBR adhesives have relatively low surface energy and therefore can be used as general-purpose adhesive to joint several substrates.

The characteristic properties of SBR-based adhesives include the following.

1. Excellent water and moisture resistance.
2. Poor tack. The addition of low-molecular-weight polymers and plasticizers or the addition of tackifiers is mandatory to obtain adequate tack.
3. Excellent flexibility.
4. Poor resistance to oils and organic solvents.
5. Poor aging. This is due to the existence of double carbon–carbon bonds. However, aging is better than for NR.
6. Low cost. Emulsion SBRs are inexpensive compared with most synthetic rubbers.
7. Wide substrate range. SBRs stick to most surfaces, including polyolefins.

The major ingredients suggested for SBR-based adhesives are listed as follows.

1. *Tackifiers.* SBRs have poor tack, so the addition of tackifiers is necessary. The tackifier increases the wetting and also increases the glass transition temperature of the adhesive. Typical tackifiers for SBR adhesives are rosins, aromatic hydrocarbon resins, alpha–pinene, coumarone–indene, and phenolic resins.
2. *Plasticizers/oils.* They are added for several reasons: (i) to improve the compatibility between SBR and the other additives; (ii) as an extender (to reduce cost); (iii) to soften the SBR; and (iv) to change the wetting properties. The most common additives are organic phosphates, phthalate esters, and aromatic hydrocarbon oils.
3. *Solvents.* Solvents are added for the same purposes as oils and plasticizers and may interact with the substrate (e.g., by partially dissolving the substrate surface). Aromatic and polar solvents are the most suitable.
4. *Fillers.* Calcium carbonate, clays, and silicas are the most typical fillers for SBR adhesives. Barite can be added to increase density. Color can be controlled by the addition of titanium dioxide, carbon black, or iron oxides.
5. *Stabilizers.* Antioxidants provide protection against UV light and thermal oxidative degradation. Hindered phenols are the most common nonstaining antioxidants.

Specific formulations of SBR adhesives can be found in Chapter 12 of *Handbook of Adhesives*, 3rd edition (Van Nostrand Reinhold, New York, 1990).

SBR adhesives can be used as pressure-sensitive label and tape adhesives. *SBR latex* is mainly used in the tufted carpet industry. SBR-based dispersion PSAs are recommended for special tapes, masking tapes, deep freeze labels, PP tapes, paper tapes, brush cleaning tapes, and double-side-coated tapes. Carboxylated SBR latex is compounded with up to 500 phr of calcium carbonate or limestone to secure the tufts in the backing and as an adhesive for the secondary backing. The adhesive is normally dried under IR lamps or using hot-air circulating ovens. SBR latices can also be used in laminating or doubling operations in textile, packaging, and automotive industries.

Solid SBR finds major use as PSAs. Solvent-borne SBRs are widely used as a high-viscosity product for bonding flooring to joists and panels to studs, thereby reducing the amount of nailing and alleviating floor squeaks. Sprayable adhesives for tire building

and retreading and the bonding of expanding polystyrene (solvent should be carefully selected to avoid cell collapse in polystyrene) are two major applications. The adhesive must always be applied to the two surfaces to be joined and it should be evaporated before or during the bonding process.

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3

Block Copolymer-Based Hot-Melt Pressure-Sensitive Adhesives

3.1 Introduction **3**-1
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3.1 Introduction

Pressure-sensitive adhesives (PSAs) based on block copolymers have comprised an area of fast growth over the past 20 years (see also Chapter 8). The unique properties of this class of adhesives rely on the structure and morphology of block copolymers. Typical block copolymers have an *A–B–A* triblock structure, where *A* is a hard end-block that has a high glass transition temperature (T_g), well above room temperature, and *B* is a soft, elastomeric mid-block with a T_g much lower than room temperature. The most common block copolymer type is styrenic block copolymers (SBC), such as styrene–isoprene–styrene (SIS) and styrene–butadiene–styrene (SBS). More recently, acrylic block copolymers (ABC) became commercially available. ABC expand the block copolymer technology to a wide range of PSA applications. For both styrenic and acrylic block copolymers, the hard *A* block and the soft *B* block have sufficiently different solubility parameters such that they are not thermodynamically compatible with each other. As a result, block copolymer-based adhesives have a unique microphase-separated morphology, where *A* blocks form a hard phase embedded in a soft, continuous phase composed of *B* blocks. The *B* mid-block phase provides viscoelastic properties and the *A* end-block phase serves as physical cross-linking domains to render cohesive strength at room temperature. The physical cross-linking mechanism is thermo-reversible. At temperatures

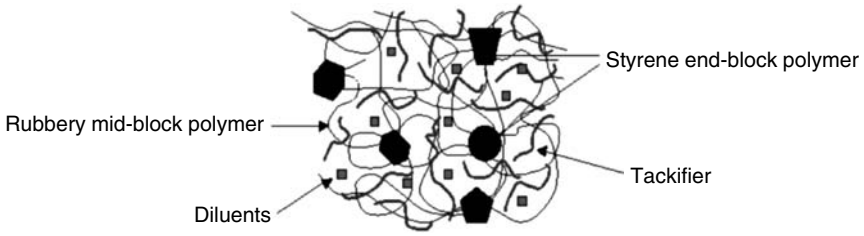


FIGURE 3.1 Schematic drawing of a microphase-separated block copolymer-based PSA.

that are high above the T_g of the end-block polymer, ordered structure disappears and the polymer turns into a viscous melt. Owing to the overall lower molecular weight, the melt viscosity is significantly lower than that of traditional rubbery polymers, such as natural rubber (NR), butyl rubber (BR), and nitrile rubber. The low melt viscosity makes it possible to process block copolymer-based adhesives in a solvent-free, hot-melt form. Besides block copolymers, tackifier resins, plasticizers, and antioxidants are also key ingredients in hot-melt PSAs (HMPSAs; see also Chapter 8). To achieve the best PSA performance, tackifier resins and plasticizers are preferably compatible with the mid-block phase, as schematically depicted in Figure 3.1.

The emergence of block copolymers greatly stimulated the growth of the HMPSA business. Nowadays, SBC-based PSAs are extensively used in label and tape constructions for many end-use applications. ABC-based hot melts are being introduced to PSA applications with the advantages of high clarity, high moisture vapor transmission rate (MVTR), and good ultraviolet (UV) resistance (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

3.1.1 Styrenic Block Copolymer-Based Hot-Melt Pressure-Sensitive Adhesives

It has been more than 40 years since Shell Chemical Company first commercialized styrenic block copolymers [1]. The early objective of developing SBCs was to make synthetic tire rubber. Since their first introduction to the market in 1965 [2], SBCs have become one of the largest base polymers for the PSA industry. They have been widely used to formulate 100% solids HMPSAs, and solution rubber-based PSAs. Throughout the years, SBC polymers have replaced NR in many PSA applications to become the dominant polymer class in rubber-based PSAs.

For styrenic block copolymers, polystyrene is the end-block and the rubbery mid-block is usually polyisoprene (PI), polybutadiene, or their saturated counterparts, polyethylene (PE)–propylene (PP) and polyethylene–butylene. The resultant SBCs are called SIS, SBS, styrene–ethylene–propylene (SEPS), and styrene–ethylene–butene (SEBS), respectively. In the following sections, the properties of the neat SBC polymers are first introduced. The SBC-based hot-melt PSAs (HMPSAs) are covered next, with detailed discussion on formulation principles, rheological and tensile properties, and the functions of the major ingredients.

3.1.1.1 Neat Styrenic Block Copolymers

3.1.1.1.1 Synthesis of Styrene Block Copolymer Polymers

The unsaturated SBCs, such as SIS and SBS, are made from living anionic polymerization in solvent. Butyl lithium is commonly used as the initiator [3]. Coupling reaction and sequential polymerization are the two major synthesis routes adopted in making commercial SBC grades. A coupling reaction was first utilized to make commercial SIS and SBS polymers. In this process, one styrene block (*A*) is first polymerized, and then the isoprene or butadiene mid-block (*B*) is added onto one end of the styrene block to form a SI or SB diblock polymer (*A*–*B*). In the next step, a divalent coupling agent such as 1,2-dibromoethane is added to connect the two diblocks by linking the isoprene or butadiene chains together. The resultant *A*–*B*–*A* triblock polymer is symmetric with identical *A* blocks on each end. It is important to note that the coupling efficiency can never achieve 100%; thus, a certain level of residual diblock content (~5%) is always present. Conventional coupling agents produce by-products such as lithium halide salts, which usually cannot be removed completely. The trace of salt is prone to generate color upon thermal aging. New coupling agent systems are being developed to improve color and thermal stability [4].

The sequential process, as its name implies, synthesizes an *A* block, a *B* block, and then the final *A* block, sequentially. Theoretically, asymmetric triblocks with styrene end-blocks having two different molecular weights can be made. The sequential process eliminates all diblock and yields a pure triblock copolymer. In addition, the final polymer is reported to be more color stable because no coupling agent is employed and, consequently, no salt by-product is present [5]. Although a pure triblock can provide maximum strength at a given molecular weight and styrene content, in many cases, some diblock is still favored to tailor adhesive performance. For this purpose, SI or SB diblock can be precisely added into SIS or SBS triblocks at the desired ratio (see also Chapter 8). Many commercial SIS and SBS grades made from the sequential process are actually physical blends of tri- and diblock polymers.

The multiblock process is another route for the production of SBCs. It is a trade secret process commercialized by Firestone that produces a multiblock architecture *A*–*B*–*A*–*B*–*A*. It produces a "tapered" SBS block copolymer in which the transition between the butadiene block and the styrene block is not sharp. Multiblock SBS typically have a broader molecular weight distribution (M_w/M_n~2) than those made from other anionic processes, which are in the range of 1.05 to 1.1 [4]. Stereon 840A (57 parts butadiene and 43 parts styrene) is an example of a commercial SBS grade made from the multiblock process.

Other modifications to SBC polymers include functionalizing SIS with hydroxyl groups [6] and using acrylic oligomers to modify anionically polymerized SBCs. The acrylic oligomers contain at least one functional group such as ester, carboxylic acid, anhydride, or epoxy [7]. The introduction of these functional groups considerably enhances adhesion to polar substrates and broadens the compatibility of SBCs with other polymers and tackifiers. Kraton Polymer LLC has also developed functionalized block copolymers, but for a different purpose [8]. They first prepare isoprene and butadiene diblock copolymers through a sequential process and then selectively hydrogenate almost all double bonds in the butadiene blocks and some of the double

bonds in the isoprene blocks. The remaining unsaturated double bonds are epoxidized. Further cross-linking through the epoxy functionality provides the needed adhesive strength, typically through UV-initiated cationic cure [9,10] (see also Chapters 1 and 8). An example of epoxidized block copolymer from Kraton is EKP-207.

SEBS and SEPS are made by further hydrogenation of the mid-block from SBS and SIS, respectively. To minimize the crystallization of the ethylene–butylene mid-block, SEBS is typically hydrogenated from a high vinyl SBS. Owing to the saturation of the polymer backbone chains, SEBS and SEPS are much more stable under UV and thermal aging. But the extra step of hydrogenation adds manufacturing cost. Compared with SIS and SBS, the saturated SEPS and SEBS polymers are not prevalent polymer choices for HMPSAs.

3.1.1.1.2 Architecture: Linear versus Radial (Multiarms)

In the coupling process, if a multivalent coupling agent is employed, a three-arm or four-arm block copolymer is produced [11,12]. These multiarm polymers are generally termed "radial" block copolymers. Radial polymers are used to improve cohesive strength and creep resistance. Radial polymers also tend to maintain better stability in melt viscosity than the linear SBCs [13].

Radial styrene–butadiene copolymers, $(SB)_n$, were commercialized in 1973 [11]. A typical example of a tetravalent coupling agent is silicone tetrachloride ($SiCl_4$), which is able to couple four diblock anions to form a predominantly four-arm radial SBS. Radial SIS, however, is more difficult to make. The bulky isopropenyl anions have too much steric hindrance to anchor simultaneously onto the four reactive sites of the coupling agent. Although using a tetravalent coupling agent, the resulting radial SIS is rarely four-arm; most commonly, the principle component is a three-arm polymer. Dexco has a patented end-capping technique [14,15] to make predominantly four-arm SIS. The SI anions are first end capped with a small amount of butadiene block, and then the resulting S–I–B copolymers are reacted with a tetravalent coupling agent to form a four-arm radial SIS.

Polymers with more than 4 arms can be obtained by terminating the chains with a multifunctional cross-linking monomer, such as a divinylbenzene [16,17] or a cyclosiloxane [18,19]. Polymers obtained by this method typically contain 8–12 arms. These materials are generally called "star" polymers.

A star polymer was developed by Kraton LLC specifically for radiation cure based on SIS (Kraton 1320X) [20–23]. Initially proposed for electron beam (EB) cure, it also cures rapidly by UV due to its very high molecular weight (M_w) (~1 million Da). This material, however, did not gain significant commercial acceptance. Subsequently, it was found that high cure rates could also be obtained from a radial SBS with high vinyl content (Kraton KX-222C) [10,24]. The vinyl groups (1,2-polymerized butadiene) are more reactive toward free radical cross-linking than internal double bonds (1,4 addition) or those of PI. Again, the multiarm structure provides lower viscosity at higher molecular weight and, thus, faster cure.

3.1.1.1.3 Molecular Weight and Entanglement Molecular Weight

Most commercially available SBC polymers are made from living anionic polymerization. The anionic process is precisely controlled and yields polymers with almost the

same chain length. The total molecular weight of SBC polymers is a controlling parameter to balance between maximum strength and good processability. A molecular weight that is too low leads to insufficient mechanical strength and poor creep/shear resistance; on the contrary, a molecular weight that is too high results in ultrahigh melt viscosity and unsatisfactory processability. The preferred total molecular weight of SBC polymers ranges from 50,000 to 500,000 Da, as determined by gel permeation chromatography (GPC) against polystyrene (Pst) standards. The molecular weight of each individual block also influences the properties of the polymer, as well as the formulated adhesive. For commercial SBC grades, the styrene end-block is generally atactic and, thus, amorphous. Its molecular weight mostly ranges from 10,000 to 20,000 Da [5], which is close to or less than the entanglement molecular weight (M_e) of atactic polystyrene, 18,000 Da. The entanglement molecular weight of a random coiled polymer is defined as the molecular weight between the entanglement points, which serve as virtual cross-links. When number average molecular weight (M_n) is less than M_e, T_g of the styrene block is strongly dependent on the actual molecular weight. The lower the actual molecular weight, the lower the T_g, as illustrated below [25],

$$T_g = T_{g_0} - \frac{K}{M_n} \tag{3.1}$$

where T_{g_0} is the glass transition for infinite molecular weight and K is a constant characteristic of each polymer.

Meanwhile, the T_g of the end-block directly correlates to its softening point and the maximum service temperature of the block copolymer. General speaking, increasing the molecular weight of the styrene block helps improve the heat resistance of the SBC-based adhesives.

The entanglement molecular weight of the common mid-block polymers is much lower than the M_e of Pst, as illustrated in Table 3.1. In practice, the molecular weight of the mid-block is usually much higher than its M_e; thus, the mid-block T_g is essentially independent of its actual molecular weight. By comparing the M_e of isoprene, butadiene, and their saturated counterparts, ethylene–butylene and ethylene–PP, isoprene has the highest M_e, which means that its rubbery plateau modulus is the lowest, as illustrated in Figure 3.2.

TABLE 3.1 Entanglement Molecular Weight (M_e), and T_g of SBC Polymers

	Entanglement Molecular Weight (M_e) (Da)	Block T_g (°C)
Styrene	18,000	100
Isoprene	7,000	−60
Butadiene	1,700	−85
Ethylene–butylene	~1,700	−55
Ethylene–PP	1,660	−55

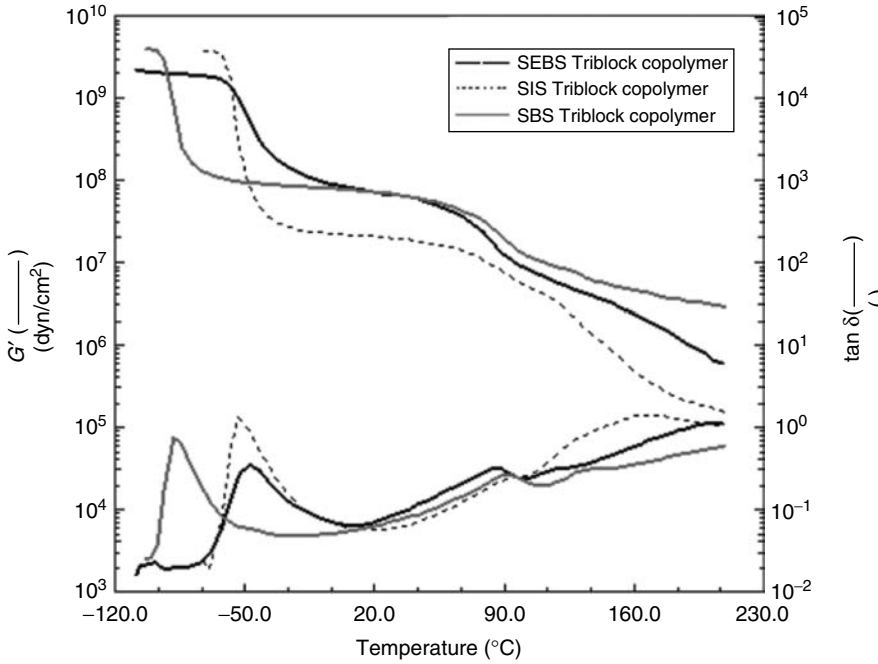


FIGURE 3.2 The elastic modulus, G', and phase angle tan δ as a function of temperature for SEBS, SIS, and SBS polymers with 30% styrene end-block.

3.1.1.1.4 Commercial Styrene Block Copolymer Grades

The commercial grades of SBC polymers offer a wide range of choices in molecular weight, styrene content, linear and radial architectures, and triblock/diblock ratio. The broad range of SBC grades provides versatility in formulating adhesives with tailored performance. Table 3.2 lists some of the major suppliers and commercial grades of SBCs on the market. All these commercial grades are supplied in nontacky powder, dense pellet, porous pellet, or crumb form. A small amount of antiblocking agents, like talc or silica, is typically added to prevent the aggregation of polymer pellets.

3.1.1.2 Formulated Styrenic Hot-Melt Pressure-Sensitive Adhesives (SHM)

3.1.1.2.1 Basic Formulation Principles

According to the definition of the Pressure-Sensitive Tape Council (PSTC) [26], a PSA is permanently tacky in dry form and can firmly adhere to a substrate with very light pressure. The adhesive requires no activation by solvent, water, or heat to exert sufficient cohesive holding power. Empirically, it was found that materials that exhibit pressure sensitivity are those that are sufficiently soft, exhibiting an elastic modulus of less than 3×10^5 Pa (3×10^6 dyn/cm^2) on a 1-s time scale at the test temperature. This somewhat surprising but well accepted empirical criterion was first established by Dahlquist [27] and is commonly

TABLE 3.2 Supplier and Trade Name of SBC

Polymer	Supplier	Trade Name
SIS, SBS	Kraton	Kraton
SEBS	Kraton	Kraton G
SIBS (isoprene–butadiene)	Kraton	Kraton
SIS, SBS	LCY	Globalprene
SIS, SBS	Dexco	Vector
SIS, SBS	TSR	Taipol
SIS	Zeon	Quintac
SBS	Firestone	Stereon
SBS	Dynasol	Dynasol
SIBS (isobutylene)	Kaneka	SIBStar
SEPS, SEBS, SEBPS	Kuraray	Septon
SBS, SEBS, SBBS	Asahi-Kasei	Asaprene, Tuftec

referred as the "Dahlquist criterion." According to this criterion, the SBC polymers are not sufficiently compliant at room temperature to be utilized as PSAs because of their high elastic modulus (Figure 3.2). Therefore, low-molecular-weight tackifiers and plasticizers are blended into the SBC polymers to dilute polymer entanglements and thus reduce the elastic modulus. Blending SBC polymers with low-molecular-weight diluents also reduces melt viscosity, thus enhancing thermal processability [28] (see also Chapter 10). A typical SBC-based SHMPSA formulation comprises 20–40% SBC polymers, 30–75% tackifiers, 10–25% diluents, and a very small amount (<2%) of antioxidants. Unlike solution or emulsion acrylic PSA systems, in which the majority component is polymer, the SHMPSAs contain multiple ingredients, among which more than 60% are tackifiers and plasticizers (see also Chapter 8). How to select the types of polymers, tackifiers, and diluents and formulate them into useful compositions not only is an art, but also requires a fundamental understanding of mechanical properties, morphology, and viscoelasticity of the SHM adhesives. In principle, formulating a good SHM to achieve a set of adhesion targets requires the following.

- Understanding the function of each ingredient and its role and contribution to the final adhesive performance
- Understanding the phase-separated mechanism of SHM and the compatibility of the multiple ingredients in each block phase
- Understanding the rheological behavior, tensile properties, and their correlations to adhesive performance such as peel, instant tack, shear resistance, and high temperature performance

Practically, rheology measurements and tensile tests are commonly used as guiding tools to aid in formulation design (see also *Fundamentals of Pressure Sensitivity*, Chapters 1, 4, and 5). The knowledge of viscoelastic properties at small deformation as well as stress–strain behavior helps the formulators to predict adhesive performance and to minimize time-consuming performance tests.

3.1.1.2.2 Rheology Measurement

Rheology measures a material's response to stress. The SHM adhesives are viscoelastic materials that possess both solid-like and liquid-like features. Deformation of a

viscoelastic material involves two mechanisms, the elastic distortion and the viscous flow: the storage modulus, G', measures the energy stored by the adhesive and is directly related to the elasticity; viscous flow and damping is reflected by the loss modulus, G'' (see also *Fundamentals of Pressure Sensitivity*, Chapters 4 and 5, and *Applications of Pressure-Sensitive Products*, Chapter 8). From the change of storage modulus, G', loss modulus, G'', and phase angle tan δ ($\equiv G''/G'$) as a function of temperature or frequency, we obtain information related to the fundamental characteristics of polymeric materials such as molecular weight, molecular weight distribution, glass transition temperature (T_g), melting point (T_m), rubbery plateau modulus, effect of cross-linker and crystallization, and compatibility of polymer blends.

Controlled strain rheology is commonly used to measure the viscoelastic response of adhesive materials at low deformation (within the linear viscoelastic limit). The method applies a small amplitude strain sinusoidally and measures the resultant rheologic response of stress and its phase with respect to oscillatory strain. Typical oscillatory rheology measurements include temperature sweep and frequency sweep. In general, the modulus at low frequency (bonding) is related to the wetting properties of the SHMs, whereas the modulus at high frequency (debonding) correlates more to the peel and tack performance of the adhesives [29], see also *Fundamentals of Pressure-Sensitivity*, Chapter 5.

Figure 3.3 illustrates the general shape of a temperature sweep curve of a SHM adhesive plotting storage modulus G' and phase angle tan δ versus temperature. When the temperature changes, the rheological response of the adhesive goes through four major regions: the glassy region, glass transition region, rubbery plateau region, and melt flow region.

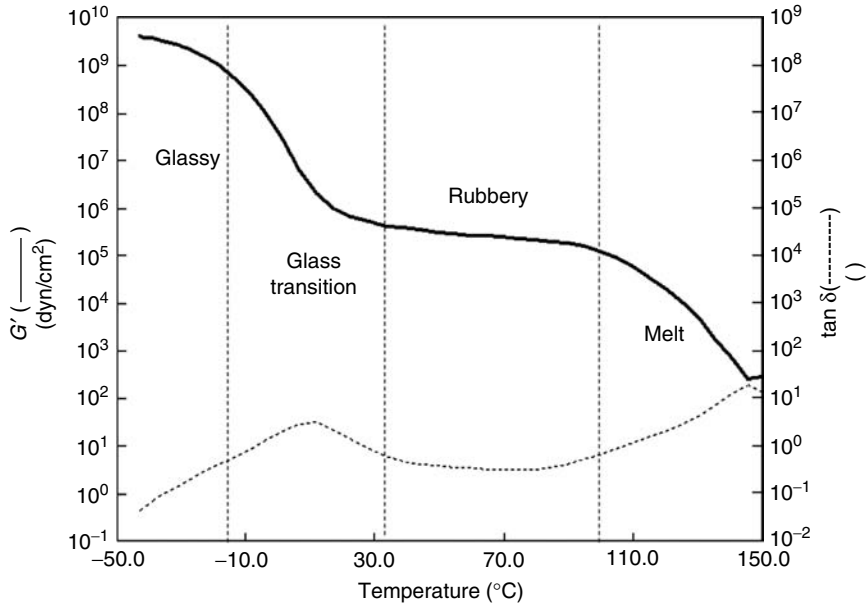


FIGURE 3.3 The elastic modulus, G', and phase angle tan δ as a function of temperature for a typical SHM adhesive.

In the glassy state, the polymer chains are frozen and all SHMs have similar modulus, on the order of 10^8 Pa. Owing to this high modulus, adhesives in the glassy state are not tacky and have no PSA properties. The glass transition region is where the adhesive transforms from the glassy state to the rubbery state. Its mechanical behavior changes drastically. Practically, the temperature at the peak of tan δ is defined as the glass transition temperature (T_g) of the adhesive. The height of the tan δ peak correlates to the viscous loss and adhesive tack, and the breadth of the tan δ peak correlates with the application window of the SHMPSAs, that is, the temperature range over which good PSA properties are obtained (see also *Fundamentals of Pressure-Sensitivity*, Chapter 5). The magnitude of the rubbery plateau modulus is determined by the entanglement molecular weight of the midblock polymer, its concentration, and the concentration of the styrene end-block. The addition of tackifiers and diluents will decrease the modulus significantly because the dilution increases the spacing between polymer entanglements. The length of the rubbery plateau is controlled by the T_g of the styrene hard domain. The higher the styrene molecular weight, the higher the T_g of the end-blocks. Therefore, a longer rubbery plateau can be achieved by using a polymer with higher styrene molecular weight. When the temperature is above the glass transition temperature of the styrene domain, the adhesive starts to flow. Storage modulus G' decreases significantly and tan δ is well above 1. The adhesive behaves more like a viscous melt. The temperature at which G' equals G'' (tan $\delta = 1$) indicates the upper limit of the use temperature. This so-called crossover temperature has a good correlation to the softening point and shear adhesion failure temperature (SAFT) of the adhesive [30].

Compared with other types of PSAs, such as solution acrylic PSAs or emulsion acrylic PSAs, the rheological behavior of SHMs has several distinctive features, as illustrated in Figure 3.4. First, the peak of tan δ (T_g) of SHMs is usually higher and its width is much narrower than that of the acrylic-based PSAs. Originally, the T_g of the SBC polymer was lower than that of the acrylic polymers, but through tackification, the T_g of the SHMs has been shifted toward a higher temperature. As a result, SHMPSAs tend to show more aggressive room temperature adhesion, but have relatively poor adhesion at extremely low temperatures compared with solution and emulsion acrylic PSAs. The narrow T_g can be attributed to the uniform chain length and isomeric compositions of SBC polymers made by the anionic polymerization process. Second, the length of the modulus plateau of those random acrylic polymers is determined by their actual molecular weight. A slightly cross-linked acrylic polymer has a very long modulus plateau and thus maintains its stiffness at high temperatures. For SBC-based adhesives, the total molecular weight of the block copolymer is much lower for good melt processability, and the length of the modulus plateau is mainly controlled by the T_g of the styrene end domain. Compared to solution or emulsion acrylic-based PSAs, the length of the rubbery plateau of SHMs is much shorter, and the cross-over temperature is lower. Consequently, typical SHMPSAs have less heat resistance.

Controlled strain oscillatory measurements such as temperature and frequency sweep tests have their limitations (see also *Applications of Pressure-Sensitive Products*, Chapter 8). They are designed for small strain within the linear viscoelastic region, where modulus is independent of strain. The maximum strain measured by most temperature sweep tests for hot-melt adhesives is generally $<30\%$. But in many real applications, the deformation of the adhesive may be well beyond the maximum strain limit.

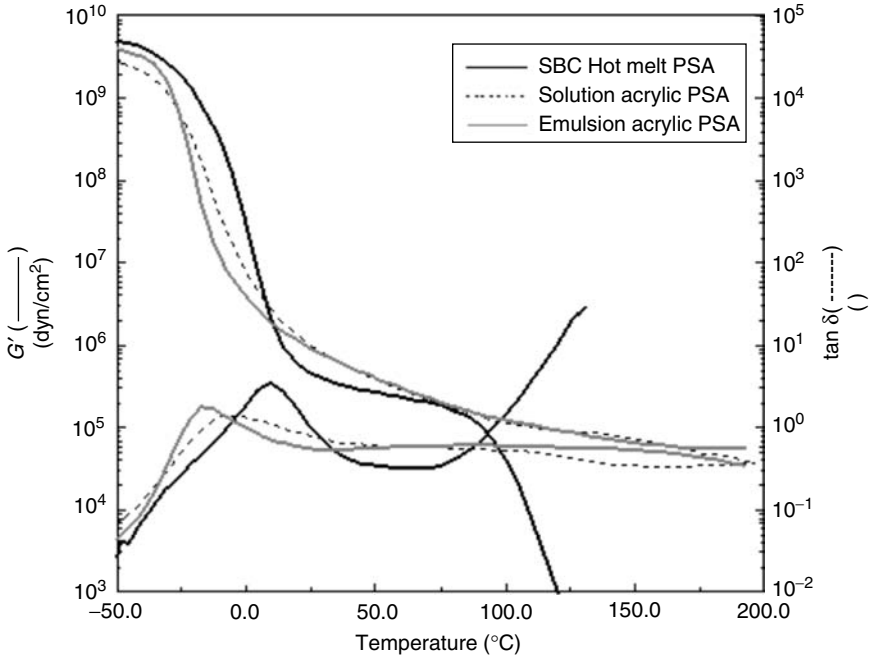


FIGURE 3.4 The elastic modulus, G', and phase angle tan δ as a function of temperature for (1) an SBC-based PSA, solid lines; (2) a solution acrylic PSA, dotted lines; and (3) an emulsion acrylic PSA, gray lines.

Normal peeling of an adhesive is one such situation. Measurements of the deformation at the peel front have indicated that deformations are commonly several hundred percent, and often up to 1000% (10 times) [31]. Where cohesive failure occurs, deformations can be even larger. In such cases, the controlled strain rheology tests are not sufficient to capture the full profile of the adhesive characteristics.

Controlled stress rheology has been employed to assess creep behavior into the nonlinear region. For instance, SHM-1 and SHM-2 exhibited very close peel and loop tack results. Both hot melts have similar formulations, except for the triblock/diblock ratio. SHM-1 has a higher diblock content, with a tri/di ratio of 30:70, whereas SHM-2 has a ratio of about 60:40. In most formulations (e.g., Figure 3.12, discussed later), the effects of high diblock content would stand out even in such a temperature scan of the linear viscoelastic properties. But in this case, the difference in tri/diblock ratio cannot be clearly differentiated from the temperature dependence of G' and tan δ, primarily due to the use of a high-molecular-weight diblock polymer with tapered structure in SHM-1. The temperature sweep profiles of the two adhesives are very similar, as illustrated in Figure 3.5. However, in a load-bearing application requiring creep resistance, SHM-2 performed much better than SHM-1. A controlled stress creep test was designed to mimic the flow behavior of adhesives under a representative shear stress (see also *Fundamentals of Pressure-Sensitivity*, Chapters 1, 8, and 9). In this test, a constant

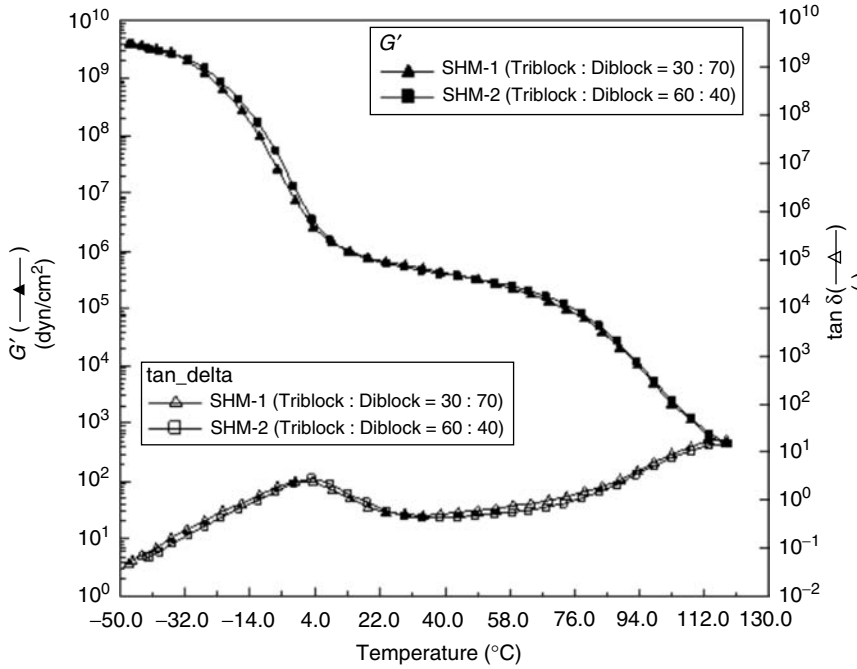


FIGURE 3.5 The elastic modulus, G', and phase angle tan δ as a function of temperature for (1) SBC-based PSA in which the tri/diblock ratio is 30:70, triangles; and (2) SBC-based PSA in which the tri/diblock ratio is 60:40, squares.

stress of 15 kPa was first applied to the adhesive for a period of time, and the resulting strain was recorded. The stress was then removed and the elastic part of the adhesive started to remove the imposed strain. This strain recovery was also recorded. Figure 3.6 illustrates the creep and recovery results of SHM-1 and SHM-2 adhesives. The difference between the two adhesives can be clearly distinguished. SHM-1 adhesive creeps much more under constant shear stress and has more unrecoverable strain due to the irreversible flow of the diblock polymers. This test indicates that SHM-1 adhesive should wet-out better on many substrates, but has relatively poorer creep performance than the SHM-2 adhesive.

Although we have talked about the PSA wet-out in terms of resistance to flow of the adhesive itself, we have not discussed the thermodynamic driving force for this flow. It is important to recognize that the driving force for elimination of air exposure at solid surfaces is always working in favor of PSA wet-out, regardless of the nature of the surface and of the adhesive. This driving force is given by [32]

$$\frac{\text{Free Energy Change}}{\text{Area}} = -\gamma_{a,air}(1+\cos\theta) \tag{3.2}$$

where $\gamma_{a,air}$ is the surface energy of the adhesive and θ is the contact angle the adhesive makes with the substrate. The higher the surface energy of the adhesive and the lower

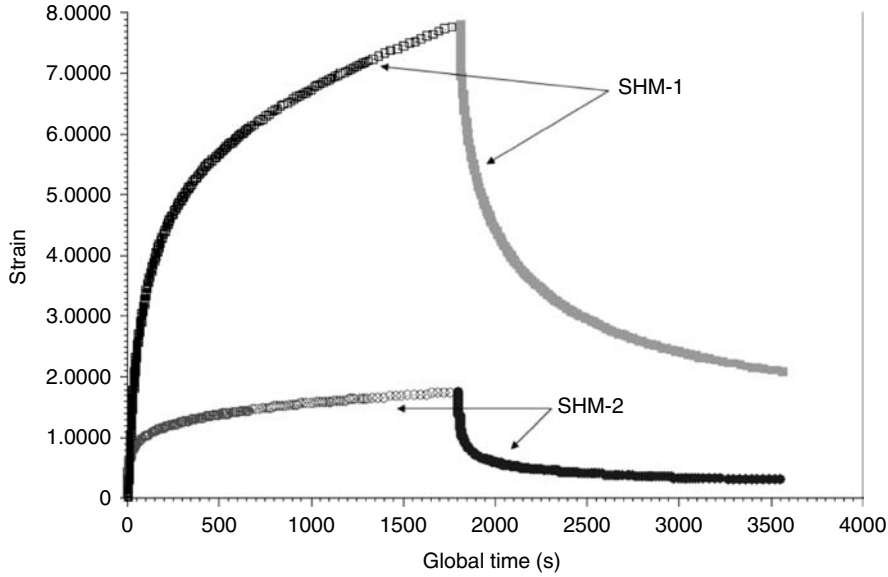


FIGURE 3.6 Creep and recovery curves of (1) a high diblock SBC-based PSA (tri/diblock ratio is 30:70) and (2) a lower diblock SBC-based PSA (tri/diblock ratio is 60:40).

the contact angle with the surface, the stronger the driving force. Only a 180° contact angle produces no driving force.

3.1.1.2.3 Tensile Test

Monotonic strain-to-failure tests are another widely used mechanical analysis that provides information such as modulus, yield stress, ultimate strength, and toughness of adhesives. Typical tests include the tensile test, flexural test, and compression test. Among those tests, the tensile test is commonly used to evaluate the mechanical properties for HMPSA adhesives (see also *Applications of Pressure-Sensitive Products*, Chapter 8). The tensile test involves pulling a dog-bone-shape specimen using an Instron Tensile Tester at a specified strain rate, typically 30.5 cm/min. Tensile properties depend heavily on temperature and test speed. The viscoelastic adhesive behaves very differently when it is above or below its glass transition temperature. Generally, like most other types of PSAs, a SHMPSA has a T_g below room temperature. Therefore, its stress–strain curve looks more similar to a low T_g ductile polymer. A schematic stress–strain curve of a SHM adhesive at relatively small deformation is illustrated in Figure 3.7.

The initial slope of stress over strain gives the modulus, which depends on the test speed or rate of strain. The higher the test speed, the higher the modulus. The deformation in this region can be recovered fully, as described by Hooke's law. At larger deformation, the adhesive goes through a yield point at which the adhesive is no longer purely elastic. Beyond the yield point, the deformation cannot be fully recovered after the stress is removed. When deformation increases, eventually the adhesive cannot sustain the stress and will break. The stress at the break point is called stress at break (σ_B) and its

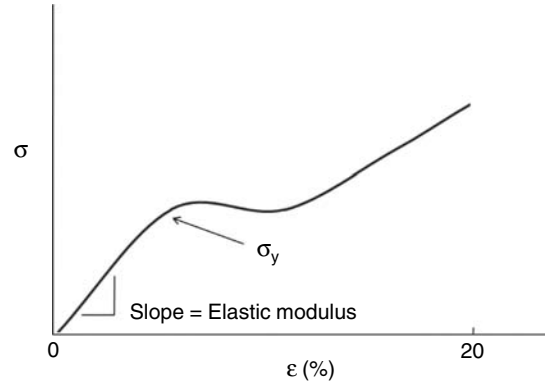


FIGURE 3.7 Schematic stress–strain curve of a SHM adhesive.

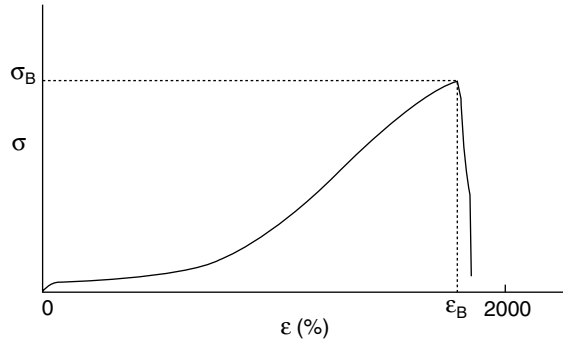


FIGURE 3.8 Stress–strain curve of a commercial SHM adhesive.

corresponding elongation is called strain at break, or ultimate elongation (ε_B). Figure 3.8 illustrates an actual tensile curve of a commercial SHM adhesive. It can be stretched to almost 2,000% of its original length. Its toughness can be measured by the area under its stress–strain curve. This area correlates to energy dissipation and impacts peel force and adhesive tack.

Other than temperature and test speed, tensile behavior can be impacted by many adhesive variables, such as molecular weight, cross-linking, crystallization, molecular orientation, copolymerization, plasticization, and polymer block morphology. For solution or emulsion acrylic PSAs, tensile properties mainly correlate to molecular weight, copolymerization, and the degree of cross-linking. However, for SBC-based HMPSAs, tensile properties depend more on the soft block–hard block physical cross-linking mechanism and the plasticization by the addition of tackifiers and diluents. For triblock SIS or SBS polymers, the aggregation of the styrene hard domain makes the rubbery mid-block act as a cross-linked system. If some of the triblock polymers are replaced with diblock polymers, the cross-linking density will be reduced, and the tensile strength will be reduced accordingly [25]. The styrene hard blocks not only serve as

a physical cross-linking agent, but also behave like rigid fillers in a continuous rubbery phase. Therefore, as the concentration of the hard blocks (either styrene block or the high softening point end-block tackifiers) increases, the filler content increases and the adhesive becomes stiffer. Correspondingly, the elastic modulus, peak stress, and stress at break increase. On the other hand, the ultimate elongation is more dependent on the mid-block polymer molecular weight. For a triblock copolymer, both chain ends of the mid-block polymer are physically cross-linked by the styrene domain. The molecular weight of the mid-block determines the spacing between the cross-links. Decreasing the mid-block molecular weight results in a reduced ultimate elongation. The addition of tackifiers and plasticizers decreases the modulus and yield stress significantly by diluting and disentangling polymer chains (see also Chapter 8).

3.1.1.3 Role of Ingredients in Pressure-Sensitive Adhesive Formulations

We have discussed the general principles in formulating SHM adhesives and demonstrated typical rheological behavior and tensile properties. Next, we will look at the role of each major ingredient and discuss its impact on the dynamic mechanical properties of the adhesive and, furthermore, how it changes the PSA performance such as peel resistance, instant tack, shear/holding power, and heat resistance.

3.1.1.3.1 Polymers

Among all the ingredients, the SBC polymer is the most critical. More precisely, it is the core of the adhesive formulation. Commercial SBC polymers offer a wide variety of choices with different melt index (MI), styrene content, coupling efficiency, diblock–triblock ratio, radial and linear structures, isoprene mid-block versus butadiene mid-block, etc. The broad range of polymer grades provides versatility for the formulators to design HMPSAs for very diverse performance requirements.

In general, high M_w or low MI polymers provide high cohesive strength, but cause a much higher melt viscosity. In addition, the high M_w is not favorable to mixing with other polymers and tackifiers from the entropy of mixing point of view. If the styrene–rubber ratio remains the same, as the overall molecular weight increases, both styrene end-block M_w and rubbery mid-block M_w increase. Creep resistance and high heat resistance will be improved as a result of increased styrene end-block M_w. A higher mid-block M_w will also improve creep resistance and lead to a larger ultimate elongation. For example, Figure 3.9 presents a comparison of the storage modulus, G', of two SBS-based adhesives versus temperature. The two adhesives, SHM-A and SHM-B, have the same formulation and composition, as illustrated in Table 3.3, except that SHM-A uses a medium M_w SBS (MI = 6, 30% styrene) and SHM-B uses a high M_w SBS (MI $<$ 1, 30% styrene). As the molecular weight of SBS increases, particularly as the molecular weight of styrene block increases, the modulus plateau of the adhesive is much longer and the cross-over temperature at which $\tan \delta = 1$ increases as a result of higher styrene T_g. The rheological profile indicates excellent heat resistance of SHM-B.

Table 3.4 compares the PSA performance. As expected, SHM-B has a significantly higher SAFT, which corresponds well to its higher cross-over temperature. However, because of the overall higher molecular weight, the melt viscosity of SHM-B at 177°C is four times higher than its lower molecular weight counterpart. SHM-B shows good peel

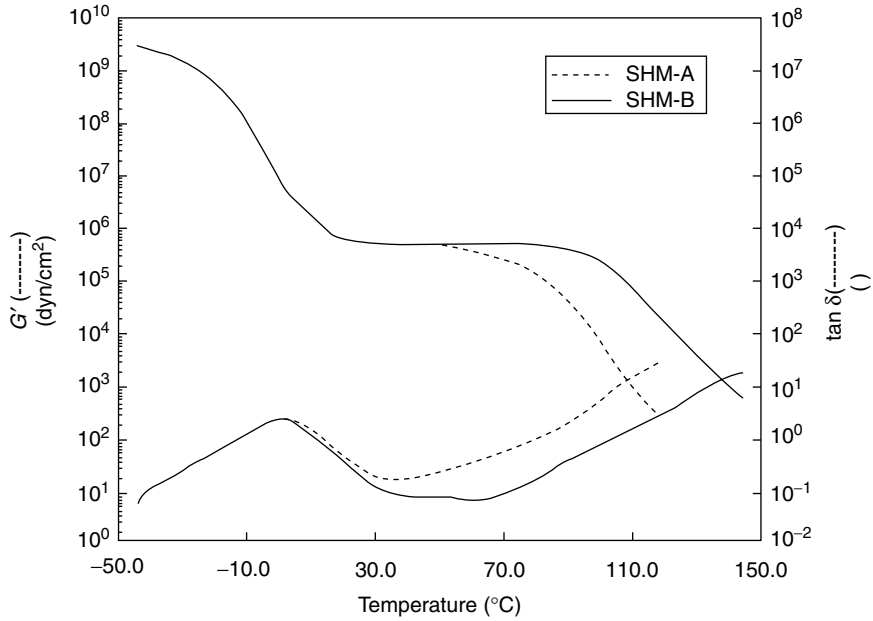


FIGURE 3.9 Temperature sweep comparison of SHM-A and SHM-B.

TABLE 3.3 Formula of SHM-A and SHM-B

	SHM-A (%)	SHM-B (%)
SBS (MI = 6)	30.0	
SBS (MI < 1)		30.0
Tackifier	69.65	69.65
AO	0.35	0.35

TABLE 3.4 PSA Performance of SHM-A and SHM-B

	SHM-A	SHM-B
Melt Viscosity @ 177°C (Pa · s)	5.4	23.4
Cross-over temperature (°C) (tan δ = 1)	83	107
SAFT (°C)	88	106
20-min peel on SS (N/m)	893	876
24-h peel on SS (N/m)	928	858
Loop tack (SS) (g/cm²)	176	225
30 KPa shear (SS) (h)	>410	>410

resistance and tack, along with excellent high heat resistance, but it is not easily processable because of its high melt viscosity.

Styrene content in a SBC grade is a critical factor that impacts tensile properties and adhesive performance. Typically, SIS grades have styrene content ranging from 14 to 35%. For SBS grades, because the solubility parameter difference between butadiene and

styrene is much smaller, 30% styrene is usually needed to ensure sufficient phase separation between the mid-block and the end-block phases. Therefore, standard SBS grades have about 30–45% styrene. It is reported that increasing styrene content increases holding power and SAFT; however, it also affects adhesive compliance and wetting properties [33]. Figure 3.10 presents a comparison of the stress–strain behavior of three SHMPSAs that use SIS grades with various styrene contents. All other ingredients and compositions are the same. The three SIS grades are pure triblock copolymers that contain 44, 30, and 18% styrene, respectively. Adhesive tensile properties such as modulus, yield stress, peak stress, peak strain, and strain at break are summarized in Table 3.5. Because the yield points of all three adhesives cannot be clearly identified, the stress at

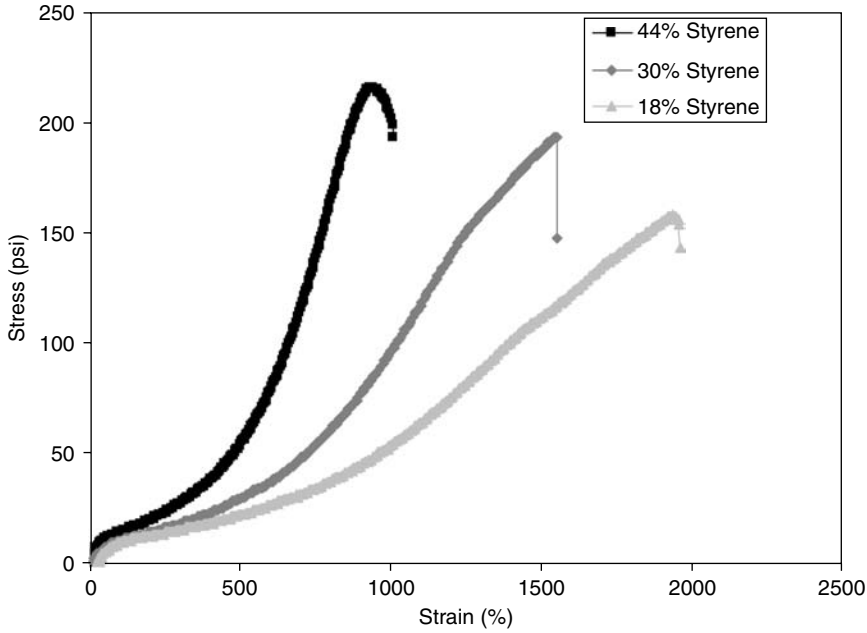


FIGURE 3.10 Stress and strain behavior of three SHM adhesives containing SIS polymers with varying levels of styrene content: (1) 44% styrene, MI = 40, squares; (2) 30% styrene, MI = 14, diamonds; and (3) 18% styrene, MI = 11, triangles.

TABLE 3.5 Tensile Property Comparison of Three SHMPSAs

Base Polymer	SIS (MI = 40)	SIS (MI = 14)	SIS (MI = 11)
SIS styrene content	44% styrene	30% styrene	18% styrene
Elastic modulus (Pa × 10^4)	36.3	15.4	8.8
Stress at 100% strain (Pa × 10^4) (~yield point)	9.2	7.3	7.0
Peak stress (Pa × 10^4)	148.9	133.1	108.9
Strain at peak (%)	936	1545	1937
Strain at break (%)	1015	1559	1963

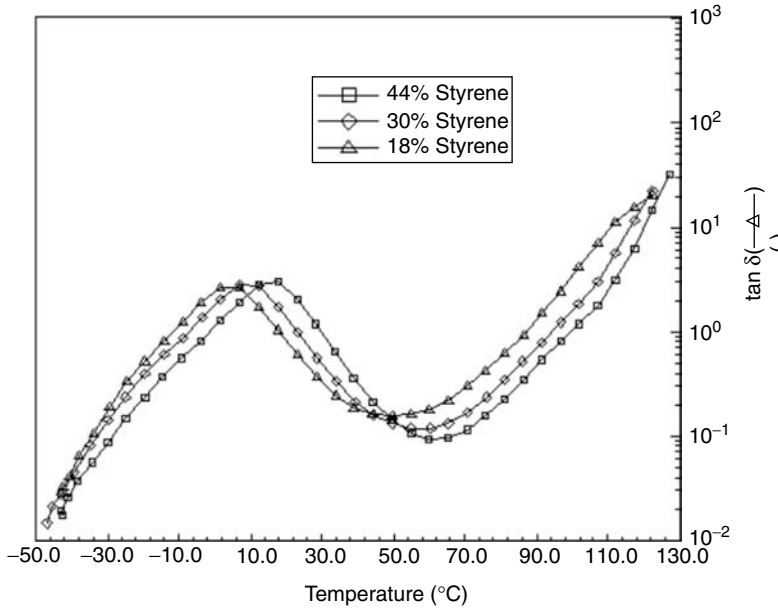


FIGURE 3.11 The phase angle tan δ as a function of temperature for three SHM adhesives containing SIS polymers with varying levels of styrene content: (1) 44% styrene, MI = 40, squares; (2) 30% styrene, MI = 14, diamonds; and (3) 18% styrene, MI = 11, triangles.

100% strain has been used as a close approximation to yield stress. For similar molecular weight, when styrene content increases, elastic modulus and peak stress increases accordingly; however, the shorter mid-block leads to a smaller strain at break. Using high styrene content, SIS can improve creep resistance, but may retard deformation and wet-out onto the bonding surface. A balance between cohesive strength and compliance is critical for good PSA performance.

The rheological profiles (tan δ vs temperature) of these three SHMPSAs are compared in Figure 3.11. In this particular formula, the SHM with 44% styrene SIS demonstrates a much higher cross-over temperature (where tan δ = 1) than the other two SHMs using lower styrene SIS. Apparently, high styrene content improves the heat resistance of the adhesives. On the other hand, a high styrene polymer has less mid-block content. Therefore, as illustrated in Figure 3.11, the impact of tackifier and plasticizer to the mid-block T_g is most significant when 44% styrene SIS is used. Its mid-block T_g has been shifted toward a much higher temperature compared with the other two polymers. The high tackifier/mid-block ratio may shift T_g of the adhesive outside the PSA window.

The ratio of diblock and triblock is another key control parameter that has been commonly used to balance flow property and cohesive strength. The diblock provides loose isoprene or butadiene chain ends that are not restrained by the styrene domain; thus, the diblock polymer does not participate in the physically cross-linked network. Therefore, its presence reduces the mechanical strength of the final adhesive. But on the other hand, the diblock can be viewed as an inherently compatible, high-molecular-weight

diluent that helps dissipate energy and enhances the flow property, which is desirable for PSAs. The commercial SBC polymer grades offer a range of diblock content from 0 to more than 80%. The pure triblock polymers with no diblock present form a strong cross-linking network, which provides excellent tensile strength and shear strength. Low-diblock-content or no-diblock SBC polymers are preferred for tape applications that require extremely high cohesive strength and high heat resistance. However, for many labeling applications, pure triblock polymers are too elastic and may not have sufficient compliance to bond well to various substrates (see also Chapter 8). The diblock is then introduced to blend in with triblock polymers to raise compliance at longer times or higher temperatures. Figure 3.12 demonstrates the impact of diblock content on storage modulus and tan δ in SBS-based SHM adhesives. In this case, when the diblock content increases from 20 to 67%, the plateau modulus declines and the adhesive is much softer. Correspondingly, tan δ increases significantly as an indication of high viscous loss. The cross-over temperature is shifted to a lower temperature, which implies a lower SAFT and softening point. The rheological behavior matches well with the PSA performance. Figure 3.13 presents a comparison of the peel resistance, loop tack, and holding power (static shear performance) of the above-mentioned two SBS adhesives. Both adhesives have comparable peel resistance, but the one with higher diblock percentage shows higher loop tack, more peel build-up, and much reduced holding power. This example clearly demonstrates the benefit of diblock content in improving wet-out and instant

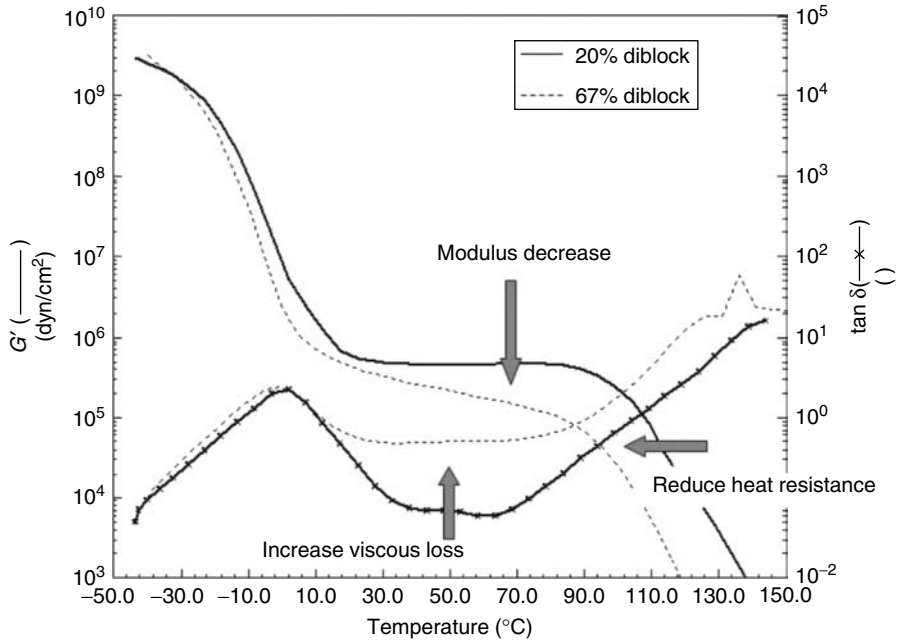


FIGURE 3.12 Rheologic profile of two SHM adhesives containing SBS polymers with varying levels of diblock content: (1) 67% diblock, dotted lines; and (2) 20% diblock, solid lines.

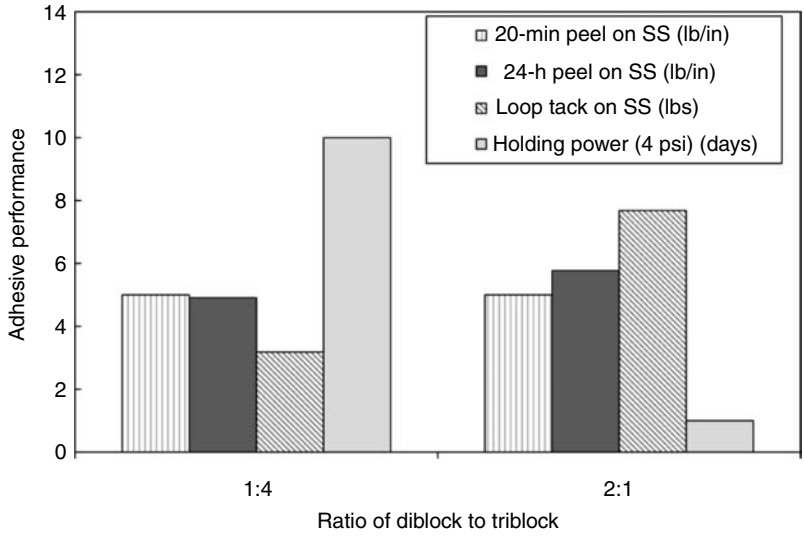


FIGURE 3.13 PSA performance of the two SHM adhesives containing SBS polymers with varying levels of diblock content.

tack. However, the addition of more diblock makes the adhesive softer and less shear resistant; it loses some degree of high-temperature performance as well.

The architecture of the polymer chains, whether they have a linear, radial, or tapered structure, also impacts the physical properties and performance of the formulated SHMs. Given the same molecular weight, radial SBC-based SHMs tend to have lower viscosity than those based on linear polymers. For instance, Raykovitz et al. [34] reported that high-styrene-content (greater than 35%), radial SBS block copolymer-based adhesive formulations were able to provide high tensile strength and very low viscosity characteristics for disposable applications. In another case, Schmidt and Puletti [35] utilized tapered SBS polymers to formulate SHMs for a disposable diaper construction application [35]. The resultant adhesives possessed superior bonding strength, and their melt viscosity was well controlled to enable a lower application temperature.

Isoprene and butadiene are the two most common mid-block monomers for adhesive use. Historically, SIS dominates in SHM adhesives for PSA applications for several reasons, as follows.

1. Higher entanglement molecular weight (M_e). Because of high M_e, SIS has a lower modulus and lower viscosity at the same molecular weight. Therefore, more SIS polymer can be added to the adhesive formulation to achieve the desired modulus while maintaining a processable viscosity. The higher polymer content provides better adhesive performance since polymer is the backbone of the adhesive.
2. Lower solubility parameter. The lower solubility parameter of isoprene versus butadiene facilitates selective tackification of the mid-block, thus maintaining heat resistance and cohesion, as discussed further below.

3. Less prone to gelation. The SIS polymer has a predominantly chain scission degradation mechanism, which minimizes cross-linking and consequent gelation. Gel particles must be avoided to provide smooth, uniform, and streak-free PSA coatings.

SIS has been prevalent for HMPSA adhesives for quite a long time. However, the cost of SIS increased rapidly over the past 5 years. This makes the easily accessible and lower cost SBS polymer more attractive to replacing some or all SIS in PSA applications. In most of the adhesive formulations, SIS cannot be directly replaced by SBS, part by part. Because polybutadiene has a higher solubility parameter than that of PI, the SBS mid-block is not compatible with purely aliphatic tackifiers. Aromatic modification of 20–30% by weight is typically required. These and other more polar tackifiers, such as rosin and its derivatives, are partially compatible with the styrene end-block and may compromise its integrity, reducing its strength and softening point. Keeping these considerations in mind, many HMPSAs have been commercialized based on SBS or blends with SIS. Kraton Polymer LLC recently developed a new family of SBC polymer that features a hybrid isoprene/butadiene mid-block (SIBS), which has demonstrated an adhesive performance equivalent to that of SIS [36]. The new SIBS polymer has been reported to have higher storage modulus plateau and a lower tan δ peak temperature than pure SIS. The lower cost SIBS polymer can be formulated to achieve adhesive properties comparable to those of the SIS polymer. Besides the difference in solubility parameters, the SBS polymer has a degradation mechanism that is dissimilar to the SIS polymer's chain scission mechanism. Because SBS tends to cross-link and forms gels upon high temperature aging, low processing temperature and an effective antioxidant package are key requirements for SBS-based HMPSAs. The unique structure of the SIBS polymer helps to overcome thermal instability. It has been reported that improved melt viscosity stability is observed due to the dual degradation mechanism of chain scission and cross-linking of SIBS polymers. Viscosity retention of a SIBS (Kraton MD6460)-based hot melt after 24 h at 160°C is significantly better than that achieved using a SIS (Kraton D1165)-based adhesive [36].

Another family of commercial SBC polymer is the saturated SEBS and SEPS polymers. Because of hydrogenation, the saturated SBC polymers possess improved resistance to oxidation and degradation. On the other hand, the nonpolar nature of the olefinic mid-block confines the selection of tackifiers. By mixing a SIS polymer with a SEBS polymer, Butch and Puletti combined the advantageous properties of good adhesion and superior heat resistance for tape applications, especially closure tapes for disposable diapers [37]. In another case, high-molecular-weight SEBS or SEPS [38] demonstrates excellent oil retention and can be formulated as an oil gel-type adhesive for dermal applications.

3.1.1.3.2 Tackifier Resins

Tackifiers are high-T_g, low-molecular-weight amorphous resins that usually compose the highest percentage in a SHM formulation. The addition of tackifiers generally reduces the plateau modulus, increases the T_g of the amorphous mid-block phase, and

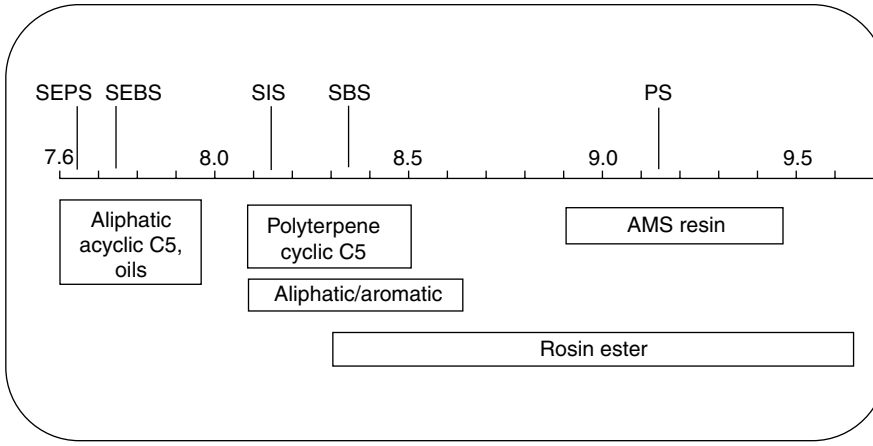


FIGURE 3.14 Schematic chart of solubility parameters of common tackifier types and SBC polymers.

reduces the melt viscosity. Tackifiers have a considerable impact on wet-out, tack, heat resistance, and processability (see also Chapter 8).

Hundreds of tackifier grades are commercially available on the market. How to select the appropriate tackifiers requires an understanding of the key characteristics of tackifiers, among which the foremost in importance is their compatibility to a specific polymer phase. Compatibility with a polymer can be determined by matching solubility parameters. Figure 3.14 presents a schematic chart of the solubility parameters of common tackifier types and SBC polymers. In general, aliphatic resins, mixed aliphatic/aromatic resins, and polyterpene resins are good choices for an isoprene mid-block; mixed aliphatic/aromatic resins, and aromatic modified polyterpene resins are suitable for butadiene mid-blocks; and the high softening point aromatic resins are more commonly used for the styrene end-block. Rosin and its derivatives have a much broader compatibility with both isoprene/butadiene mid-blocks and styrene end-blocks due to their high solvency power.

A simple way to test compatibility is to dissolve an equal amount of tackifier and polymer in a solvent such as toluene and then cast a film to check the clarity of the blend. An incompatible polymer–tackifier blend typically loses clarity and tackiness. The compatibility of the tackifier and polymer can be further confirmed by rheological tests. Two mid-block tan δ peaks usually indicate an incompatible tackifier. In some special cases, the adhesive could be still optically clear while two mid-block tan δ peaks are present, because the size of the separated phases is not large enough to be recognized as macrophase separation. But, in general, a single narrow tan δ peak with reduced plateau modulus indicates good compatibility between the tackifier and the mid-block polymer. If the tackifier is partially compatible, a broad tan δ peak is often visible.

Other than compatibility with each individual polymer phase, the concept of selective compatibility is even more crucial in formulating good PSA adhesives. A tackifier with selective compatibility to a SBC polymer usually means that it compatibilizes

very well with one polymer block, but is almost incompatible with the other polymer block. For example, some mid-block tackifiers, such as aliphatic C5 resins, have excellent compatibility to the isoprene mid-block, but have very limited compatibility to the styrene end-block (see also Chapter 8). Consequently, the C5 resins reduce the modulus of the rubbery phase very effectively and shift the mid-block T_g to a higher temperature. Meanwhile, they do not affect the cohesive strength of the styrene end-block and thus maintain the high creep resistance and high temperature resistance provided by the hard end-block. For some other applications where low melt viscosity, aggressive instant tack, and continuous wet-out are more important than high creep and heat resistance, tackifiers that have a wider compatibility range with both the mid-block and the end-block phase are more desirable. Examples of such tackifiers are rosins and rosin esters.

Figure 3.15 demonstrates the DMA temperature sweep curves of three model formulations using one SIS polymer and one oil with three various types of tackifiers at the ratio of 29:14:57. All three tackifiers have similar softening points. The aliphatic C5 resin (Wingtack 95, Cray Valley, Exton, PA) has very good selective compatibility with the isoprene mid-block. The styrene end-block T_g does not shift much due to its incompatibility with the aliphatic C5 resin. When the aliphatic tackifier is modified by aromatic components (Wingtack Extra, Cray Valley), it increases the compatibility in the styrene block and decreases the T_g of the styrene end-block domain. Rosin ester (Sylvalite 100LT, Arizona Chemical, Jacksonville, FL), is more compatible with both isoprene and styrene

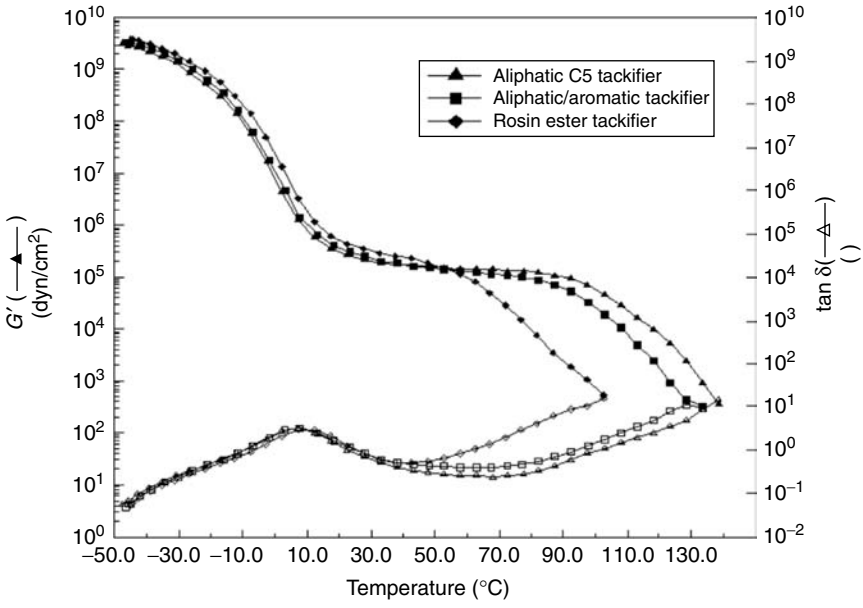


FIGURE 3.15 Tackifier effect in three model formulations (SIS:tackifier:oil = 29:57:14). (1) Aliphatic C5 tackifier, triangles; (2) aliphatic/aromatic tackifier, squares; and (3) rosin ester tackifier, diamonds.

blocks. Thus, the T_g of both mid-block and end-block phases gets closer. Compared with the other two hydrocarbon tackifiers, the rosin ester tackifier significantly reduces the T_g of the styrene phase. The resultant formulation has a much lower melt viscosity and excellent wet-out ability; whereas the use of rosin ester reduces the high-temperature resistance of the model formulation.

The softening point is another key factor to consider in selecting appropriate tackifiers because the softening point of the tackifier contributes to the T_g of the tackified polymer phase. Instead of measuring T_g, most tackifier manufacturers provide the softening point value as a key specification (see also *Applications of Pressure-Sensitive Products*, Chapter 8). The softening point measures the temperature above which the material starts to flow. Empirically, the softening point of a tackifier is about 40–45°C higher than its T_g. For a compatible polymer–tackifier–plasticizer blend, the T_g of the mid-block phase can be roughly calculated using the Fox–Flory equation shown below,

$$\frac{1}{T_{g\,\mathrm{Adh-midblock}}} = \frac{W_{\mathrm{Polymer-mid}}}{T_{g\,\mathrm{Polymer-mid}}} + \frac{W_{\mathrm{Oil}}}{T_{g\,\mathrm{Oil}}} + \sum_{j=1}^{n} \frac{W_{\mathrm{Tackifier_j}}}{T_{g\,\mathrm{Tackifier_j}}} \tag{3.3}$$

where W_i is the weight fraction of each ingredient excluding styrene content and T_{gi} is the glass transition temperature (Kelvin temperature is used here) of each component. Given that the styrene end-block forms a separate phase from the rubbery mid-block, the weight fraction of styrene should not be counted in the calculation. Thus, $W_{\mathrm{polymer\text{-}mid}}$ should only count for the weight fraction of mid-block polymer. For instance, in a formulation of 30% SIS, 20% oil, and 50% tackifier resin, if the SIS polymer comprises 70% isoprene and 30% styrene, and assuming the tackifier and oil are mainly mid-block compatible, the recalculated weight fractions W_i are 23% mid-block polymer, 22% oil, and 55% tackifier, respectively. However, this T_g calculation is just a rough estimate because, in reality, both tackifier and oil do not always go to the mid-block phase only. It is very difficult to evaluate how much tackifier and oil actually go to the mid-block and the end-block separately. However, for a given formulation this equation is very useful in predicting how changes in the proportions of ingredients will affect T_g.

Commonly used tackifiers in SHM adhesives are either naturally derived or petroleum derived. Naturally-derived resins include rosin, rosin ester, and polyterpene (see also Chapter 8). Rosin tackifiers are derived from pine stumps (wood rosin), trees (gum rosin), or paper pulp (tall oil rosin). They are acidic in nature and are a mixture of several isomers. The most common rosin acid isomer is abietic acid [39]. Because of their fused ring structure, rosins have great solvency power and can solubilize a wide variety of polymers. However, rosin acids are not stable under heat and are subject to oxidation. Other disadvantages of rosins as a tackifier include their dark color, strong odor, and short shelf life. They may also cause an allergic reaction in some people. For this reason, rosins are rarely used in hygiene and skin-contact applications (see also *Applications of Pressure-Sensitive Products*, Chapter 4). More stable derivatives of rosin can be produced by esterification, disproportionation, hydrogenation, and polymerization of the rosins. For instance, rosin esters are made by esterification of rosin with polyols such as glycerin and pentaerythritol. Different softening point rosin esters can be produced by varying polyols. Similar to pure rosins, rosin esters are compatible

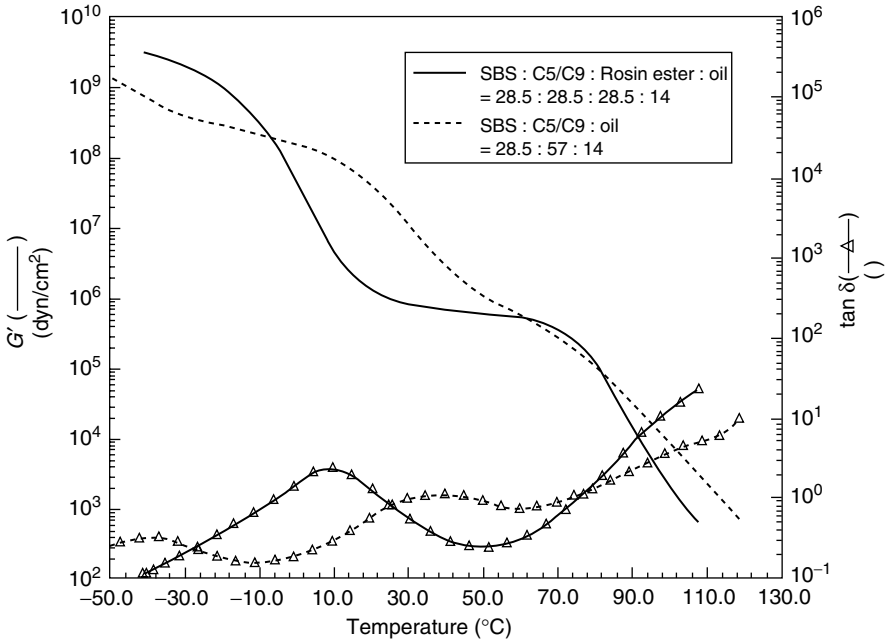


FIGURE 3.16 The elastic modulus, G', and phase angle tan δ as a function of temperature for SBS-based adhesives with and without rosin ester. (1) SBS:hydrocarbon resin:rosin ester resin: oil = 28.5:28.5:28.5:14, solid lines; and (2) SBS:rosin ester resin:oil = 28.5:57:14, dotted lines.

with a wide range of polymers with very different solubility parameters, but they are much more stable. Therefore, rosin esters have been used extensively in both SBS- and SIS-based formulations. Rosin ester tackifier can also be used as a compatibilizer for polymers and synthetic hydrocarbon tackifiers that are marginally compatible (see Chapter 8). For instance, a formulation containing SBS, C5/C9 tackifier with about 8% aromatic content, and oil is marginally compatible. The bulk adhesive is cloudy and has little tack. Its rheological behavior is illustrated with a dotted line in Figure 3.16. Two tan δ peaks are clearly seen as the evidence of multiple phase formation. Except for the mid-block and end-block phases, there is an additional tackifier-rich phase with a tan δ peak at around 40°C. If half of the low-aromaticity C5/C9 tackifier is replaced with a rosin ester, the adhesive becomes clear and tacky. Its rheological profile is illustrated by the solid line in Figure 3.16. The single mid-block tan δ peak implies good compatibility of all of the ingredients in the adhesive.

Disproportionation and hydrogenation of the rosins provide more stable and lighter color grades. The use of partially or fully hydrogenated rosin esters extends the shelf life of the SHMs and provides better stability at higher processing temperatures. For applications that require superb clarity, long time color stability, and excellent adhesion to low surface energy substrates, hydrogenated rosin esters are preferred choices. Examples of hydrogenated rosin grades are Eastman's Foralyn and Foral E rosin esters [40]. However, highly saturated rosin ester is very expensive and may crystallize over time.

TABLE 3.6 Supplier and Trade Name of Naturally Derived Tackifiers

Naturally-Derived Tackifier	Supplier	Trade Name
Polyterpene resin	Hercules (Aqualon)	Piccolyte S115
Polyterpene resin	Arizona Chemical	Sylvares ZT105
Pentaerythritol ester	Arizona Chemical	Sylvalite RE100
Pentaerythritol ester	Meadwestco	Westrez 5800
Pentaerythritol ester	Georgia-Pacific	Novares 1100
Disproportionated rosin ester	Eastman Chemical	Permalyn 6110
Glycerine ester of hydrogenated wood rosin	Hercules/Eastman	Staybelite ester 10
Hydrogenated rosin ester	Hercules/Eastman	Foral 85

Polyterpenes are derived from the by-products of wood stumps, paper pulp, and citrus oil extractions. Terpene monomers are usually mixtures of α-pinene, β-pinene, and limonene. Their cyclic structure contributes to their excellent solvency power. Polyterpenes have been used as an outstanding tackifier for NR and SBC. In addition, polyterpenes are light in color and are approved for various Food and Drug Administration (FDA)-regulated applications, including indirect food contact and direct food contact (see also *Applications of Pressure-Sensitive Products*, Chapter 8). However, in recent years, the use of polyterpenes has decreased rapidly due to the rising cost and the shortage of limonene monomer. Meanwhile, new synthetic hydrocarbon tackifiers have been developed to match the performance of polyterpene resins. As a result, adhesive manufacturers tend to use synthetic resins increasingly to replace terpene tackifiers for supply security and, in some cases, cost saving purposes. Table 3.6 lists several suppliers and trade names of naturally derived tackifiers.

Petroleum-derived tackifiers are synthetic hydrocarbon resins produced using various polymerization techniques. These polymers, like the polyterpenes, are oligomeric (far below their entanglement molecular weight) and, thus, their T_g increases with molecular weight. Their monomer feed streams come from the by-product of the oil-refining process. The most common monomers for hydrocarbon tackifiers are C5, C9, and $(C5)_2$ monomers and the corresponding resins can be classified as aliphatic C5 resins, aromatic C9 resins, and cycloaliphatic C5 resins. By copolymerizing the aliphatic or cycloaliphatic C5 monomers with C9 monomer, C5/C9 copolymer resins with a wide range of solubility parameters are produced.

Aliphatic C5 resins comprise the acyclic and cyclic types. The primary acyclic C5 monomers are *trans*- and *cis*-piperylene. The polymerized acyclic C5 resins are usually linear structures and having a softening point range from 80 to 115°C. A typical grade of acyclic C5 tackifier is Wingtack 95 (Cray Valley). Another C5 grade, under the trade name Wingtack 10 (Cray Valley), is a liquid resin with a softening point at 10°C. These C5 resins are also referred to as synthetic polyterpenes because of their similarity to the natural sourced polyterpene resins in color, polarity, and excellent solvency [39]. The cyclic C5 resins are polymerized from cyclic dienes $(C5)_2$, primarily dicyclopentadiene (DCPD), to form a variety of ring structures. Subsequently, the unsaturated double bonds in DCPD resin can be hydrogenated to produce a very stable, water white, odorless tackifier class for applications that require clarity and excellent thermal and UV stability.

The pure aliphatic hydrocarbon tackifiers have excellent solubility with the isoprene mid-block, but have limited compatibility with the butadiene mid-block. To improve butadiene mid-block compatibility, a copolymer of aliphatic C5 and aromatic C9 molecules is made by blending the two monomer feed streams. Typically, the primary component is aliphatic and the aromatic content could range from 5–35% by weight. The varying aromaticity in the copolymer mix changes the solubility parameter, polarity, and compatibility to both mid-block and end-block. Increasing the aromatic content could improve butadiene compatibility, but would weaken the styrene end-block. Figure 3.17 illustrates examples of a SBS polymer with three hydrocarbon tackifiers with increasing aromaticity. The SBS polymer is D1102 from Kraton; the three hydrocarbon tackifiers are Wingtack 95 (C5 resin, Cray Valley), Wingtack Extra (C5/C9 copolymer, Cray Valley), and Wingtack 86 (C5/C9 copolymer, Cray Valley). Kaydol oil (a paraffinic oil) is added to all three formulas in the same amount. Figure 3.17 presents a comparison of the storage modulus G' and tan δ versus temperature of all three formulations. The samples of SBS with Wingtack 95 (no aromaticity) and Wingtack Extra (low aromaticity) are cloudy due to macrophase separation. The two tan δ peaks confirm the incompatibility of the polybutadiene mid-block with the primarily aliphatic tackifiers. On the other hand, the sample containing SBS and Wingtack 86 is clear and tacky. Wingtack 86 has relatively higher aromaticity and thus has an overall higher solubility parameter. The aromatic content in Wingtack 86 significantly improves its compatibility with the polybutadiene mid-block. Only one mid-block tan δ peak is observed and the plateau modulus is reduced.

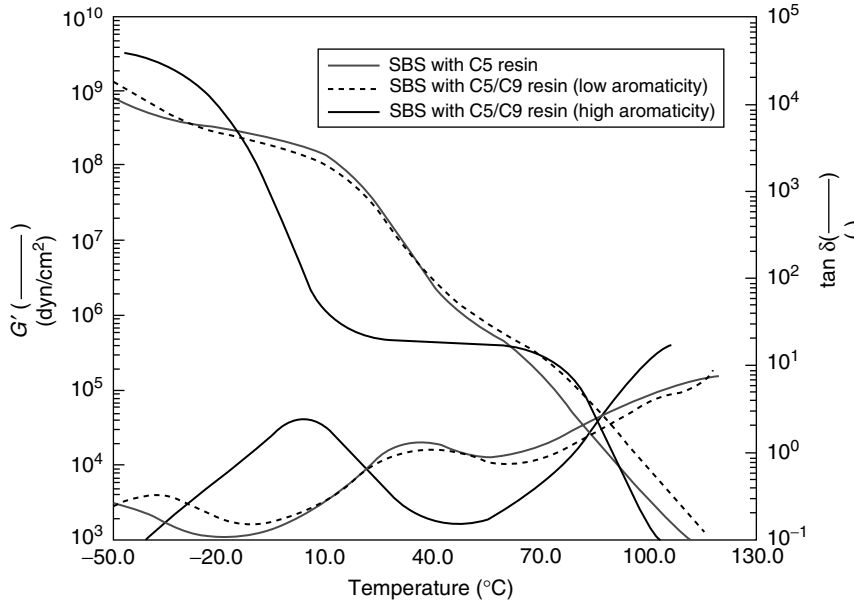


FIGURE 3.17 The elastic modulus, G', and phase angle tan δ as a function of temperature for SBS-based adhesives containing hydrocarbon tackifiers with varying aromatic contents.

Generally speaking, rosin ester, polyterpene, aliphatic C5, and aliphatic C5/aromatic C9 copolymer resins are preferably compatible with the rubbery mid-block and are usually regarded as "mid-block tackifiers." On the other hand, tackifiers that are used to reinforce the styrene end-blocks are called "end-block tackifiers." High-softening-point aromatic C9 resins or pure aromatic monomer resins are the most commonly used end-block tackifiers for PSA applications.

Owing to their similar chemical structures, aromatic C9 resins have good solubility in the styrene end-block. For a SBC, the styrene end-block provides strength and stiffness to the adhesive. The purpose of using an end-block tackifier is to strengthen the styrene end-block and to enhance the stiffness and creep resistance. Aromatic C9 resins are made from fractionation of the high aromatic petroleum stream and contain a crude mixture of aromatic monomers. They are usually darker in color and have a strong petroleum odor, which limits their usage.

Another type of aromatic end-block tackifier is pure monomer resins. They are made by polymerization of the nearly pure indene, α-methyl styrene, or vinyl toluene monomers. The pure monomer aromatic resins are almost water white and have an imperceptible odor. They have excellent clarity and stability like the hydrogenated resins [41]. In addition, the pure nature and low color allows the pure monomer resins to comply with FDA direct food contact regulations. Not surprisingly, the pure monomer resins are more expensive.

Aromatic end-block tackifiers generally have a high softening point, ranging from 85 to 160°C. Typically, the higher the softening point, the higher the molecular weight. If a high softening point aromatic resin is selected, only a small amount of addition in the formula is preferred (usually less than 10%) to minimize viscosity and avoid phase separation. Excessive end-block tackifier will separate from the styrene matrix and form an individual tackifier phase acting like fillers, which could significantly increase the melt viscosity and reduce the adhesive tack and clarity. Aromatic end-block tackifiers have been used frequently in disposable diaper adhesives to offer higher creep resistance and improved cohesion [34]. The use of aromatic pure monomer resins also allows a lower amount of polymer to be used while achieving the same level of cohesion as a high-polymer-content adhesive with the benefit of lower viscosity [42]. Table 3.7 lists several suppliers and trade names of petroleum-derived tackifiers.

Molecular weight, color, polarity, and hydrogenation are also important characteristics to take into account. For the same chemical structure, a lower molecular weight

TABLE 3.7 Supplier and Trade Name of Petroleum-Derived Tackifiers

Petroleum-Derived Tackifier	Supplier	Trade Name
Aliphatic	Cray Valley	Wingtack 95
Aliphatic	Eastman	Piccotac 1100
Aliphatic	Kolon	Hikorez A-1100
Aliphatic/aromatic	Cray Valley	Wingtack extra
Aliphatic/aromatic	Eastman	Piccotac 9095
Hydrogenated resin	Exxon	Escorez 5400
Aromatic pure monomer resin	Eastman	Kristalex 3100
Aromatic resin	Cray Valley	Norsolene S115

correlates with a lower softening point. Lower molecular weight favors the entropy of mixing and compensates for some of the unfavorable enthalpic contribution. Consequently, lower molecular weight tackifiers have broader compatibility with a wider range of polymer and other tackifiers. The color of the tackifier usually controls the color of the formulated adhesive. Hydrogenation of tackifiers provides lighter color and improved thermo-oxidative stability, but reduces the solubility parameter. Tackifiers with high polarity and functional groups can improve the specific adhesion to polar substrates.

3.1.1.3.3 Plasticizers

Plasticizers are optional for solution rubber or acrylic PSAs and extrudable PSAs; however, for remeltable SBC-based HMPSAs, plasticizers are commonly used to reduce melt viscosity so that the adhesive can be manufactured and coated at temperatures below the degradation temperature of the SBC polymers (see also Chapter 8). Plasticizers are also used to adjust mid-block T_g and to reduce raw material cost. Typical plasticizer content in a SHMPSA formulation is about 10–25%. Options of plasticizers include petroleum oils, polar plasticizers, and natural oils. For some specific applications, where oil may migrate into the face stock film or the bonding substrate, polar plasticizers such as phthalate, dibenzonate, and dimer acid [43] are the choices. Phase separation is still the major concern when polar plasticizers are used for SBC polymers. Natural oils are rarely used for HMPSAs because of their poor stability, strong odor, and high cost. Owing to the nature of the SBC polymers, petroleum-derived oils are the dominant choices. Common petroleum oils used in SHM adhesives fall into two major categories, naphthenic oil and paraffinic oil. Naphthenic oils have higher aromatic and naphthenic (i.e., cycloparaffin) content. The feed stream of the naphthenic crude has high aromatic fractions. It must go though a refining process to eliminate traces of sulfur and nitrogen and to hydrogenate most aromatics to naphthenics [4]. The level of hydrogenation determines the cleanliness and quality of the naphthenic oils. Less hydrogenated grades are regarded as "process oils." They have a pale straw color and are less expensive. Heavily hydrogenated grades are white oil and The United States Pharmacopeia (USP) grades. The major differences in these grades are their color, stability, and FDA compliance. Paraffinic oils, which also go through a hydrogenation process, tend to have more linear species and less naphthenic content in the final product. Comparatively, they are more stable and lighter in color. The paraffinic white oil grades have been extensively used in HMPSA adhesives that require better color stability and specific FDA compliance. Owing to the compositional difference, paraffinic oils have relatively lower solubility parameters and lower T_g than naphthenic oils. Consequently, they have better compatibility to the hydrogenated mid-block polymers. Because of the ring structure, naphthenic oils have a higher solvency power. In addition to the relatively high aromatic content, they have a propensity to solubilize and soften the styrene end-block. Therefore, the addition of naphthenic oils reduces heat resistance as well as softening point [4]. The molecular weight of the oils also plays a key role in viscosity, T_g, and solubility. When the molecular weight increases, as a rule of thumb, the oil viscosity and T_g rise, but the compatibility with the mid-block polymers decreases because the favorable entropy of mixing is reduced. When the amount of oil exceeds the capacity limit that mid-block polymers can hold, oil bleeding or plasticizer migration occurs. The bleed oil can cause

TABLE 3.8 Supplier and Trade Name of Paraffinic and Naphthenic Oils

Oil Type	Supplier	Trade Name
Paraffinic	Sonneborn	Kaydol
Paraffinic	Crompton	Semtol 350
Paraffinic	Crompton	Britol 35T
Paraffinic	Penreco	Drakeol 35
Naphthenic	Calumet	Calsol 5160
Naphthenic	Nynas	Nyflex 222B

staining, especially on paper face stocks, or can even form a weak adhesion layer that destroys the adhesive bond. Therefore, selecting the appropriate molecular weight and finding the closest solubility match can maximize the capability of oil retention. Table 3.8 lists several suppliers and trade names of paraffinic oil and naphthenic oil grades.

In the past, naphthenic oils were usually more economical than paraffinic oils for adhesive use, but changes in the tire industry are reversing this situation. The naphthenic oil grades used for adhesives are highly hydrogenated and have minimal aromatic fractions compared with the traditional oils used in the tire industry. However, due to new safety regulations seeking to eliminate the fraction of aromatic oil, which is carcinogenic, in tires, the demand for highly hydrogenated naphthenic oils is increasing rapidly. The supply of naphthenic oils for adhesive use is tight and the price continues to rise. As alternative options, paraffinic oils and natural oils are becoming more popular for HMPSA use.

3.1.1.3.4 Stabilizers

Stabilizers, although comprising a very small percentage of the formulation, are a very critical component in HMPSA adhesives. With the presence of oxygen, many raw components in HMPSA formulations, including SBC polymers and tackifiers, are susceptible to thermal or UV light-induced degradation if their chemical structures are not fully saturated. To ensure stability for the duration of shipping and storage, stabilizers (antioxidants) are usually added during the manufacturing of SBC polymers and tackifiers (see also Chapter 8). For SBC polymers with unsaturated double bonds, antioxidants such as hindered phenols and secondary amines are typically used to scavenge radicals and to interrupt the oxidation cycle. For tackifiers, antioxidants are commonly used to reduce the hydroperoxide formation, which is the main cause of discoloration at elevated temperatures. Stabilizers improve the stability of the raw ingredients within their shelf life; however, the level of stabilizers in the raw components is far from sufficient to protect the formulated adhesives from degradation throughout hot-melt mixing, high-temperature shearing, storage, coating, and converting processes (see also Chapter 10). Additional antioxidants are necessary for SBC-based hot-melt adhesives. For most adhesives, as well as the raw ingredients, the autooxidation cycle starts with the generation of radicals (R*) upon heat, mechanical stress, UV light, etc. Radicals form peroxy radicals (ROO*) in the presence of oxygen, which further react to form hydroperoxides (ROOH). Hydroperoxides can subsequently decompose into hydroxyl (*OH) and alkoxy radicals (RO*). This oxidation cycle is autoaccelerated and will not be terminated by

itself. The oxidation-induced degradation results in adhesive physical property changes, such as viscosity drop, discoloration, gel formation, charring, foaming, and loss of tack (see also *Applications of Pressure-Sensitive Products*, Chapter 8). To interrupt this oxidation cycle, different types of antioxidants are used to either scavenge peroxide and alkoxide radicals or decompose hydroperoxides to form more stable chemicals. The former are regarded as primary antioxidants. For instance, Irganox® 1010 (Ciba, Tarrytown, NY) is a commonly used primary antioxidant. The latter are called secondary antioxidants, which are added in combination with a primary antioxidant. Phosphites (TNPP and Irgafos 168) and thioethers or thioesters are very effective secondary antioxidant choices as hydroperoxides decomposers. Traditionally, the costabilizer system combining a primary antioxidant and a secondary antioxidant is often used to provide the maximum protection to SBC-based HMPSAs. Recently, some new multifunctional antioxidants have been commercialized with both primary and secondary antioxidant functions in one molecule. A typical example is Irganox 1726, developed by Ciba [44]. It has been reported as a very effective antioxidant for SIS- and SBS-based hot-melt adhesives. Moreover, it has excellent processing stability and good high-temperature performance.

3.1.1.4 Manufacturing

Styrenic HMPSAs are manufactured by mixing all the ingredients at temperatures above the softening temperatures of all components (see also Chapter 10). A variety of mixers are in commercial use. The common feature of these mixers is adequate power to shear the SBC polymers into a melt at temperatures below their order–disorder transition temperature (~190°C). Manufacturers of suitable mixers include Moritz, Littleford, Hockmeyer, Baker Perkins, and Brabender. The adhesive products are supplied in drums, blocks wrapped with release paper, and tack-free blocks in sealed plastic films (e.g., Easymelt™) [45]. To minimize oxidation of the polymer and tackifiers, vacuum and nitrogen protection are commonly employed during batch mixing.

3.1.1.5 End-Use of Styrenic Hot-Melt Pressure-Sensitive Adhesives

Although the original application for SBC was not adhesives, over the years SBC polymers found their home in various PSA end-use applications, particularly in hot-melt form. Compared with solvent-borne and water-borne acrylic PSAs, HMPSAs have the advantages of easy handling, low energy processing, low equipment investment, fast coating speed, versatile coat weight, low adhesive cost, and no solvent handling. Because of these benefits, SBC-based adhesives in hot-melt form have been very popular in many labeling applications, where low cost and fast coating speed are major requirements, and in tape applications, where thick coat weight is desirable (see also *Applications of Pressure-Sensitive Products*, Chapter 4). SHM adhesives also are used in medical and dermal applications (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

3.1.1.5.1 Labeling Application

SHM adhesives have been extensively used in various labeling applications, including general purpose paper labels for packages and plastic containers, dairy labels for high-density polyethylene (HDPE) milk jugs, clear labels for beer bottles and shampoo bottles, battery labels, fruit labels, tire labels, freezer labels, etc. (see also *Applications of*

Pressure-Sensitive Products, Chapter 4). For labeling applications, usually SHM adhesives are transfer coated. The adhesive is first coated onto a release liner and then laminated and transferred to the face stock (see also Chapter 10). Paper and biaxial-oriented polypropylene (BOPP) are dominant face stocks (see also *Applications of Pressure-Sensitive Products*, Chapter 1). If paper face stock is used, oil staining upon aging is a likely issue that must be addressed. The level of staining can be evaluated by an oil bleeding test (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Typically, a specimen of adhesive coating on paper is aged on both the release liner and the bonding surface at 50°C, 60°C, and 35°C/95% relative humidity conditions. A specified weight is placed on top of the sample specimen to mimic oil bleeding under stress. Sample specimens are then evaluated visually after 1 week and 1 month. A good labeling adhesive should not stain the paper or change the dimension of the face stock materials. Polyethylene terephthalate (PET) (Mylar) face stock is more expensive, so it is only used for high-end applications (see also *Applications of Pressure-Sensitive Products*, Chapter 1). Vinyl (PVC) films typically contain a large amount of plasticizer (~25%). This plasticizer may migrate into a SHM adhesive upon aging. Meanwhile, the plasticizer and tackifier in SHMs may migrate into the vinyl films as well. This two-way migration causes dimensional instability of the vinyl films. Moreover, plasticizers from the vinyl films can attack the styrene domains of the adhesive, leading to a loss of cohesion or, if not absorbed by the adhesive, plasticizer exudation from the vinyl can produce a weak boundary layer and destroy the adhesive bond. Therefore, vinyl films are rarely used as face stock for SHM adhesives (see also *Applications of Pressure-Sensitive Products*, Chapter 1).

Generally speaking, a good labeling adhesive must possess the following characteristics: excellent wetting properties on various bonding surfaces including low-surface-energy substrates; aggressive instant tack and high peel resistance; moderate shear and creep resistance; moderate heat resistance; no staining and migration to both face stock and bonding surface; no cold flow and oozing during roll storage, no shrinkage; and excellent cutting and die-cutting performance (see also *Applications of Pressure-Sensitive Products*, Chapters 4 and 8). SHMs, which can dissipate more energy, are preferred over highly elastic adhesives for labeling applications. High heat resistance and high cohesive strength are sometimes compromised to promote wetting properties. For this purpose, a diblock is often used in labeling adhesives. A diblock is also used to reduce the elasticity and thus improve the die-cutting performance in the converting process [46] (see also Chapter 8).

Because labels are applied to different substrates at different application and service temperatures and require various levels of adhesion from permanent to repositionable to removable, one type of labeling adhesive is not sufficient to meet all requirements (see also Chapter 8). A wide range of labeling adhesives is available on the market, tailored to specific end uses. For example, a low and broad mid-block T_g is a requisite for dairy label adhesives and freezer label adhesives because the adhesives are required to possess good adhesion at both lower temperatures and room temperature (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Adhesives used for fruit labels must comply with direct food contact FDA regulations. Therefore, all of the ingredients in the formulations must meet the same FDA compliance (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Paper labels for corrugated boxes must maintain

adhesion at various humidity conditions; thus, humidity resistance is a key characteristic for these adhesives. For battery labels, acid resistance and high temperature resistance are critical. Recently, clear bottle labels became popular for beer and beverages (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Clarity and color stability are important features when designing these adhesives. Moreover, for some customers who recycle bottles, labels are required to be removed during high-temperature, caustic wash cycles (see also *Applications of Pressure-Sensitive Products*, Chapter 8). More hydrophilic SHM adhesives are required to suit the customers' needs. For instance, a SBS-based adhesive comprising acid-functional diluents and high-acid-number rosin tackifiers demonstrates excellent adhesion on glass bottles and, more importantly, can be easily removed from the container during caustic wash without leaving any adhesive residue on the bottles [43] (see also Chapter 7).

3.1.1.5.2 Tape Applications

Traditionally, the tape industry relies heavily on PSAs, especially solution acrylic PSAs (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Tape applications usually require high holding power at both room temperature and elevated temperatures. As a rule of thumb, in addition to aggressive peel resistance, adhesives for tape applications must have high cohesive strength, high shear and creep resistance, and a high SAFT. Block copolymer-based HMPSAs are not a natural fit for tape applications because their cohesive strength and heat resistance are limited by the physically cross-linked styrene domain. However, on the other hand, SHM adhesives can be easily coated at a much higher coat weight (>3 mil), which is very difficult to achieve by oven drying solution acrylics at fast line speeds (see also Chapter 10). The advantageous coating characteristics of SHMs make them a preferred choice for tape applications that require moderate heat resistance and thick coating weight. For example, SHMPSAs are used in packaging tapes, road marking tapes, shipping box closure tapes, tamper-evident packaging tapes, and diaper closure tapes (see also *Applications of Pressure-Sensitive Products*, Chapter 4). From a formulation point of view, a tape-grade SHM adhesive typically comprises a triblock copolymer with no or low diblock content and relatively high M_w; a mid-block tackifier package that does not destroy the integrity of the styrene end-block, and a high softening point end-block tackifier to reinforce the styrene domain. Achieving the maximum cohesive strength at manageable viscosity is the key for a good tape-grade SHM. Ideally, the viscosity of the adhesive should be controlled at below 30 Pa · s at 160°C to ensure good coatablity and maintain normal processing temperatures. A processing temperature that is too high may induce the degradation of SHMs. Recently, research has focused on UV-curable hot-melt adhesives, which have a promising future as tape-grade adhesives. Before UV curing, the hot-melt adhesives have sufficiently low viscosity to ensure high-quality coating. After curing, ultrahigh cohesive strength is provided by these chemically cross-linked polymers (see also Chapter 8).

Medical tape is another unique tape class for dermal and transdermal applications, such as bandage tape, ostomy seals, wound dressing, and drug delivery patches (see also *Applications of Pressure-Sensitive Products*, Chapter 4). The requirements of medical tapes include good holding power on skin, prolonged wear time, and easy and painless removal after use without leaving an adhesive residue (see also *Applications of Pressure-Sensitive Products*, Chapters 5 and 6). Typically, a soft adhesive with minimal viscous loss is

TABLE 3.9 Model Formulation and Performance for Medical Application

Formulation	Parts (%) by Weight
Kraton G1651	5
Kraton G 1702	5
Mineral Oil	40
Wingtack 10	20
Kristalex 3085	15
Test	Performance
Viscosity @ 163°C	2.91 Pa · s
180° peel off HDPE (N/m)	26.3
Loop tack on SS (g/cm^2)	65.9
Skin grab	Excellent
Adhesive removal (pain)	None

preferred. Hydrogels have been used, but are associated with several disadvantages such as high cost, humidity sensitivity, and the associated requirement of special packaging (see also Chapter 7 and *Applications of Pressure-Sensitive Products*, Chapter 4). SHMs have been used to address this need. Oil–gel-type adhesives for such dermal applications consist of an ultrahigh-molecular-weight SEBS polymer, a diblock polymer, a compatible tackifier, and a high amount of liquid diluents [38,47]. Table 3.9 presents an example of an oil–gel adhesive and its skin-related performance.

3.1.2 Acrylic Block Copolymer-Based Hot-Melt Pressure-Sensitive Adhesives

Polyacrylates and poly(meth)acrylates are the most prominent chemistries used in PSA industries (see also Chapters 5 and 8). Acrylic-based PSAs have been widely used in various end-use applications where optical clarity, durability, weatherability, broad temperature adhesion, and thermal stability are required. Traditionally, acrylate polymers are random, long-chain (co)polymers prepared by either solution polymerization in organic solvents or aqueous emulsion polymerization. The solvent or water is removed during the coating process to produce the "dry" PSA (see also Chapter 10). Over the past 2 decades, more stringent environmental regulations and cost reduction needs have driven the evolution of acrylic PSAs toward 100% solid, hot-melt forms. Physical entanglement of polymer chains alone cannot provide the proper balance between high service temperature and manageable melt viscosity. For this reason, random acrylic (co)polymers have had little success as commercial hot-melt adhesives. Instead, researchers have sought: (1) ways of postcuring random copolymers by EB or UV [48–51] (see also Chapter 1) or (2) acrylic block copolymer analogs to SBCs (see also Chapter 1).

3.1.2.1 Advancement in Making Processable Acrylic-Based Hot-Melt Pressure-Sensitive Adhesives

Over the past 2 decades, researchers have actively explored new synthesis methods to make novel block acrylic polymers for processable HMPSA use. Early attempts

involved free radical synthesis, through which styrenic macromonomers or acrylic macromonomers can be grafted as pendant side chains [52–54] or comb-like structures [55,56] to soft acrylic polymer backbones to enhance shear strength in PSA compositions. In these cases, the number and the molecular weight of the high T_g, hard, grafted side chains are constrained by the balance of adhesive tack and melt viscosity. Ionomeric acrylic systems have also been investigated but found limited commercial utility due to unstable melt viscosity [57]. Further research work focused on advanced free radical synthesis. For instance, polyvalent mercaptan segments were used as a center to make radial or star-shape acrylic block copolymers via a multistep radical polymerization [58]. The *AB* or *ABA* types of acrylic block copolymers were prepared from living radical polymerization by utilizing an iniferter to initiate, control, and terminate polymerization. The term iniferter refers to a combined function as an initiator, a chain transfer agent, and a terminator [59]. Block copolymers made from iniferter polymerization tend to have broad molecular weight distribution (high polydispersity) and indistinct block/phase boundaries [60]. More recent work explored the use of anionic polymerization as an alternate means to synthesize acrylic block polymers. An initiation system composed of a functional initiator and an alkali metal alcoholate was developed for making acrylic homopolymers and block polymers anionically with narrow polydispersity and controlled tacticity [61,62]. It is also reported that *A–B–C* triblock copolymers with narrow polydispersity can be prepared by anionic polymerization using an organic alkali metal or an alkaline-earth metal as initiator [63]. Recently, Kato et al. [64] patented a production process using anionic living polymerization to prepare an *A–B–A* triblock acrylic copolymer where the *A* blocks are immiscible with the *B* blocks. As a result of this process, the first generation of commercial grade acrylic block copolymers was introduced to the market by Kuraray Co., Ltd. The acrylic block copolymers were sequentially polymerized with a very narrow molecular weight distribution (M_w/M_n = 1.1–1.3) [65].

3.1.2.2 Neat Acrylic Block Copolymers

The commercially available acrylic block copolymers from Kuraray are anionically polymerized methyl methacrylate (MMA)/butyl acrylate (BA)/MMA triblock copolymers (MAM), where MMA is the high T_g, hard end-block and BA is the soft mid-block [65]. Its form, similar to that of the SBCs, is nontacky, free-flowing pellets finished by extrusion. The pellet form is very easy to handle. It allows MAM-based hot-melt adhesives produced in the same mixing equipment for conventional SBC-based hot melts (see also Chapter 10) with no need for modification [66].

Compared with acrylic polymers made from free radical processes, the MAM polymers have a very narrow molecular weight distribution and contain very low levels of residual monomers. These features arise from the high conversion rate in the anionic reaction and the high-temperature, high-vacuum finishing process by extrusion. For instance, only about 12 ppm of BA monomer trace was found in an MAM-based formula [66]. As a comparison, 500–1000 ppm residual monomer is common for a solution acrylic PSA without special exhaustive purification treatment. Consequently, the ultralow level of residual monomers makes MAM polymers an ideal fit for medical, hygiene, and personal care applications.

Owing to saturation of the polymer backbone chains, MAM triblock copolymers outperform the conventional SBC polymers in terms of clarity and stability. The MAMs exhibit excellent resistance to oxidative and photochemical degradation, which is an intrinsic weakness of unsaturated SBC polymers. One other advantage of MAM polymers comes from their high end-block T_g. The syndiotactic MMA end-block has a T_g of around 130°C, which is significantly higher than the T_g of the styrene end-block (~100°C). Therefore, theoretically the MAM polymers can provide higher heat resistance than SBC-based PSAs. Another difference between the SBC and MAM polymers is entanglement molecular weight (M_e). The M_e of the MMA end-block is lower than that of styrene, which means the minimum MMA molecular weight and content needed to maintain a physical cross-linking end-block phase is lower. Meanwhile, the M_e of the mid-block (BA) is much higher than that of isoprene or butadiene blocks, as listed in Table 3.10. At the same mid-block molecular weight, the higher M_e of BA results in a much lower plateau modulus and yields a softer polymer. Therefore, less tackification is needed to bring the modulus of MAM polymers to below the Dahlquist criterion of 3×10^5 Pa, a requisite for pressure sensitivity. Figure 3.18 illustrates the dynamic mechanical properties of a SIS and a MMA/BA/MMA polymer with the same end-block content. Compared to the SIS polymer, the MAM polymer has a much lower plateau modulus, a slightly higher mid-block T_g, and a much higher cross-over temperature [65]. These features enable the MAM polymers to be used in applications that require softness and high heat resistance.

3.1.2.3 Formulated Acrylic Hot-Melt PSAs (AHM)

3.1.2.3.1 Tackification

The neat acrylic block copolymers are usually not pressure sensitive in nature. Tackifiers and plasticizers are usually required. A typical block AHMPSA formulation consists of 15–50% MAM polymers, 15–70% tackifiers, and 0–25% plasticizers. Given the polar nature of the acrylic block copolymers, the choice of compatible tackifiers includes rosin and their derivatives (e.g., rosin ester), aromatic hydrocarbon resins, aromatic modified hydrocarbon resins, and aromatic modified polyterpene resins. In some cases where good clarity and weatherability is critical, more color-stable tackifiers such as hydrogenated rosin ester and hydrogenated aromatic hydrocarbon resins are preferred [67]. Typical plasticizers may include fatty acid esters, polyethers, phthalates, hydrogenated rosin esters, adipate, and glutarate esters [55,67].

TABLE 3.10 Glass Transition Temperature (T_g) and Entanglement Molecular Weight (M_e) Comparison between ABC and SBC Polymer

	Block T_g (°C)	Entanglement Molecular Weight (M_e) (Da)
BA	−54	17,000
MMA (syndiotactic)	130	6,970[a]
Isoprene	−60	7,000
Butadiene	−85	1,700
Styrene	100	18,000

[a] M_e for 81% syndiotactic poly(methyl methacrylate) with 46,000 Da M_w [68].

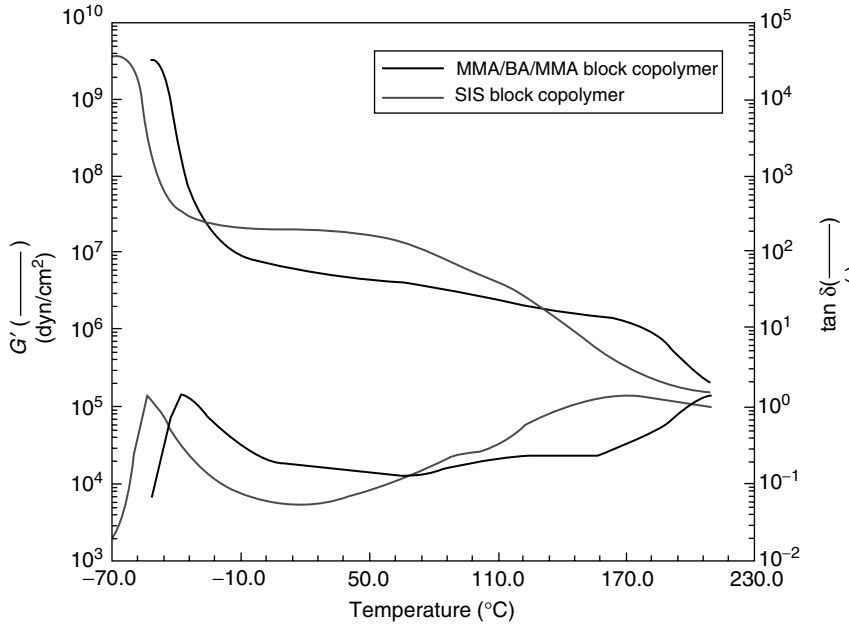


FIGURE 3.18 The elastic modulus, G', and phase angle tan δ as a function of temperature for (1) SIS block copolymer with 30% styrene, gray lines; and (2) MMA/BA/MMA block copolymer with 30% MMA, solid lines.

In a block copolymer adhesive system, as discussed before, effective tackification requires that a tackifier be compatible with one block, but partially compatible, or more preferably incompatible, with the other block. By such tackification, the mid-block and end-block are able to maintain a clear phase separation. This selective tackifier compatibility can be achieved by manipulating the solubility parameter of the tackifier in comparison to the two-block phases. If the solubility parameter difference between the mid-block and end-block is large, for example, if the styrene block and isoprene block in a SIS polymer, a wide variety of tackifiers can be used to soften the isoprene mid-block and yet have minimal impact on the styrene end-block. However, for the commercial MAM block copolymers, the solubility parameters of MMA end-block and BA mid-block are very close. This makes it challenging to find effective mid-block tackifiers that do not dilute and soften the MMA end-block.

3.1.2.3.2 Dynamic Mechanical and Tensile Properties

Through careful formulation with appropriate tackifiers that are selectively compatible to the BA mid-block, the MMA end-block can retain its strength. The high T_g of the MMA block provides superior heat resistance compared with a typical high-performance SIS-based HMPSA. Table 3.11 compares the dynamic mechanical properties (T_g, storage modulus G', and cross-over temperature) between two commercial high heat grades of SIS-based PSA and two AHM formulations. The four adhesives demonstrate

TABLE 3.11 Examples of Dynamic Mechanical Analysis Properties of SIS-Based PSAs and AHMPSAs

	PSA-A	PSA-B	PSA-C	PSA-D
Base polymer	SIS	SIS	MAM	MAM
Mid-block T_g (°C)	8.8	6.0	5.9	3.6
Cross-over temperature (°C) tan $\delta = 1$	104.1	93.4	130.5	121.7
G' at 20°C (Pa $\times 10^4$)	5.5	7.1	5.1	5.9
G' at 40°C (Pa $\times 10^4$)	2.8	3.9	1.4	2.4

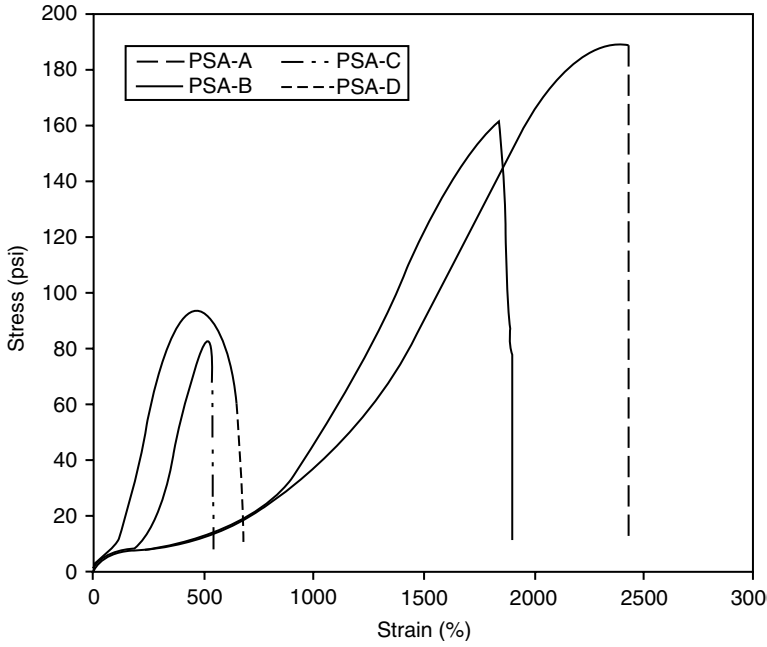


FIGURE 3.19 Stress and strain behavior of two SHM adhesives (PSA-A and PSA-B) and two AHM adhesives (PSA-C and PSA-D).

slightly varied T_g and the same magnitude of plateau modulus. However, the AHM formulations demonstrate much higher cross-over temperatures. As discussed before, cross-over temperature correlates with the softening point of the adhesives and is one of the performance indicators for heat resistance.

DMA characterizes the mechanical behavior of adhesives at small deformation (see also *Applications of Pressure-Sensitive Products*, Chapter 8). For larger deformation, tensile properties provide more information on adhesive stiffness, toughness, stretchability, and energy dissipation. Figure 3.19 illustrates the tensile properties for the same four adhesives. The difference in yield stress is not significant, but peak stress and break stress of the AHM formulations are lower. Moreover, it is noteworthy that both AHM adhesives demonstrate limited strain at break, which is only about 500–600%, whereas

TABLE 3.12 Examples of Tensile Properties of SIS-Based PSAs and AHMPSAs

	PSA-A	PSA-B	PSA-C	PSA-D
Base polymer	SIS	SIS	MAM	MAM
Yield stress (Pa × 10^4)	4.6	5.2	4.3	5.0
Stress at Break (Pa × 10^4)	86.0	129.1	49.8	46.6
Strain at break (%)	1913.5	2382.8	536.9	601.5
Peak stress (Pa × 10^4)	108.3	129.6	53.6	68.6

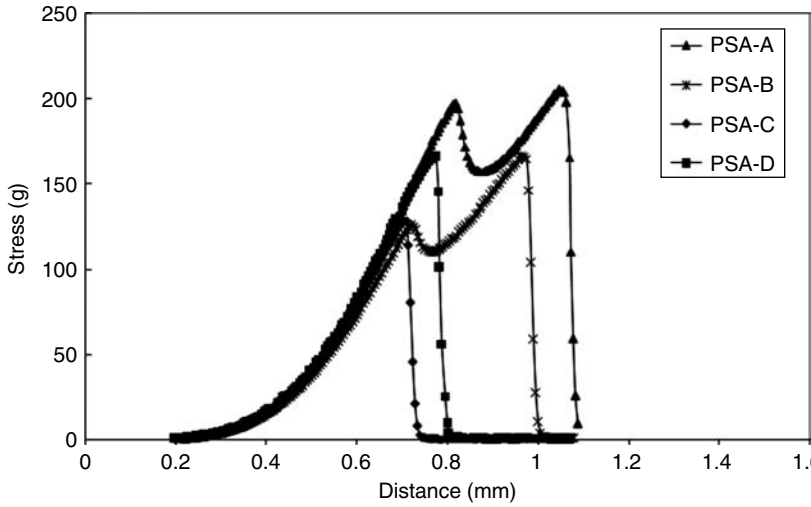


FIGURE 3.20 Probe tack adhesion of two SHM adhesives (PSA-A and PSA-B) and two AHM adhesives (PSA-C and PSA-D).

typical SBC-based adhesives can be stretched to more than 2000%, as illustrated in Table 3.12. Although the AHM adhesives demonstrate good stiffness and strength, they are less stretchable than the SBC-based hot-melt adhesives.

3.1.2.3.3 Probe Adhesion Measurement

Probe methods are commonly employed to characterize both tack and peel forces (see also *Fundamentals of Pressure Sensitivity*, Chapters 4, 6, 7, and *Applications of Pressure-Sensitive Products*, Chapter 8). In practice, a probe is used to compress the PSA adhesive with a given force for a very short dwelling time. It is then separated from the PSA adhesive at a specified speed. During debonding, the viscoelastic PSA adhesives usually form cavities that will continue to expand laterally. Then the thin walls between cavities extend into fibrils and finally get fully detached from the probe surface [69]. The maximum extension and the strength of the fibrils are determined by the energy release rate and the nonlinear elastic modulus of the adhesives [70], see also *Fundamentals of Pressure-Sensitivity*, Chapter 6. Figure 3.20 provides a comparison of probe measurements for the same four PSA adhesives. In these experiments, the stainless-steel (SS) probe pressed the adhesives at 450 *g* force for 1 s before pulling away from the adhesive

at a constant speed of 0.5 mm/s. The first peak in the curve indicates the onset of cavity formation, which is governed by the elastic properties of the adhesive. The width of the shoulder or plateau is associated with fibrillation and energy dissipation. Despite the similar initial peaks, the AHM adhesives PSA-C and PSA-D demonstrate no shoulders in their tack curves. Both adhesives are detached from the probe immediately after the cavities are formed, which implies that the interfacial fracture energy release rate is not sufficiently high to develop bulk cavitations. Crack propagation at the interface is rapid, which limits the total energy dissipation during debonding. The fibrillation and debonding mechanisms for probe methods and peel tests are almost the same when the same adherent is used. Therefore, the integral under-the-probe curves directly correlate to the peel performance [70]. Accordingly, we can predict from the curves in Figure 3.20 that AHM adhesives PSA-C and PSA-D will have lower peel resistance on SS than the two SIS-based PSAs.

3.1.2.3.4 Melt and Ultraviolet Stability

As noted previously, the neat acrylic block copolymers demonstrate excellent resistance to oxidative degradation. After dilution with tackifiers and plasticizers, the formulated AHM still maintains thermal stability and UV stability far superior to that of SIS-based adhesives. Table 3.13 compares the melt viscosity after aging at 177°C between a SIS-based hot melt (PSA-G) and two block acrylic-based formulas (PSA-E and PSA-F). After 24 h of aging at 177°C, the SIS-based adhesive loses almost 60% of its original viscosity, whereas the two block acrylic PSAs demonstrate none or less than 30% viscosity loss. Usually, the reduction in viscosity is a key sign of polymer degradation. Degradation also can lead to charring, which may foul the melt tank or the coater head. This example clearly demonstrates the improved thermal stability of AHM over the conventional SBC-based HMPSA [66].

In Table 3.14, the effects of UV exposure on adhesives are compared. Coatings of three adhesives, an exterior-grade commercial solution acrylic (PSA-H), a SIS-based hot melt (PSA-I), and an AHM (PSA-J) were exposed directly to UV light in a QUV

TABLE 3.13 Melt Viscosity before and after Aging at 177°C

Adhesives	PSA-E	PSA-F	PSA-G
Base polymer	MAM	MAM	SIS
Initial viscosity at 177°C (Pa · s)	9.9	8.2	8.9
After 24 h at 177°C (Pa · s)	7.2	8.5	3.6
% Change	−27	+4	−60
Char ring at surface	None	None	Light

TABLE 3.14 Effects of UV Exposure on Adhesives (QUV-UVA-340 bulb)

Adhesive	Type	Initial Color[a]	Time to Lose Tack[b] (h)	Color after 707 h
PSA-I	SHM (SIS)	1	<70	2
PSA-H	Solution acrylic	0	>707	0
PSA-J	AHM	0	355–707	0

[a] 0 = clear, 1 = very pale yellow, 2 = pale yellow.

[b] Samples examined after 70, 208, 355, and 707 h.

(QUV accelerated weather tester from Q-panel Lab) chamber with UVA-340 bulbs, which simulated the UV spectrum of sunlight but at a much higher intensity. Color change and tack performance were evaluated before and after UV exposure. As illustrated in Table 3.14, the SIS-based adhesive turns yellower, as expected, whereas the AHM adhesive and the solution acrylic adhesive remain colorless. In terms of tack loss, the solution acrylic PSA, which is almost pure polymer (i.e., unformulated) performs the best. The AHM adhesive retains its tackiness significantly longer than the SIS-based HMPSA under UV exposure. Because of these features, it is promising to use acrylic block copolymer-based hot-melt adhesives for graphics and exterior use.

3.1.2.4 End-Use Applications of Acrylic Hot-Melt Pressure-Sensitive Adhesives

Given the benefits that AHMPSAs are soft, clear, free of monomers, stable, and highly heat resistant, they are suitable for end-use applications such as medical, graphics, removable tapes, and many others. The crucial characteristics for adhesives used in medical applications are that they must be soft and conformable to skin; they should have good moisture permeability and painless removal. The features of AHMs fit very well with these requirements. As mentioned previously, the ABC itself has a very low plateau modulus. After proper tackification, the AHM can be formulated to be extremely soft while maintaining good heat resistance with no cold flow. By nature, the AHM can be detached from the adherent with minimum stretching and gives clean, comfortable removal from the skin. Moreover, the acrylic chemistry provides the polymer with high MVTR. A high MVTR value is critical for skin adhesives because it helps with healing and long-term wear. Figure 3.21 provides a comparison of MVTR values of two AHM

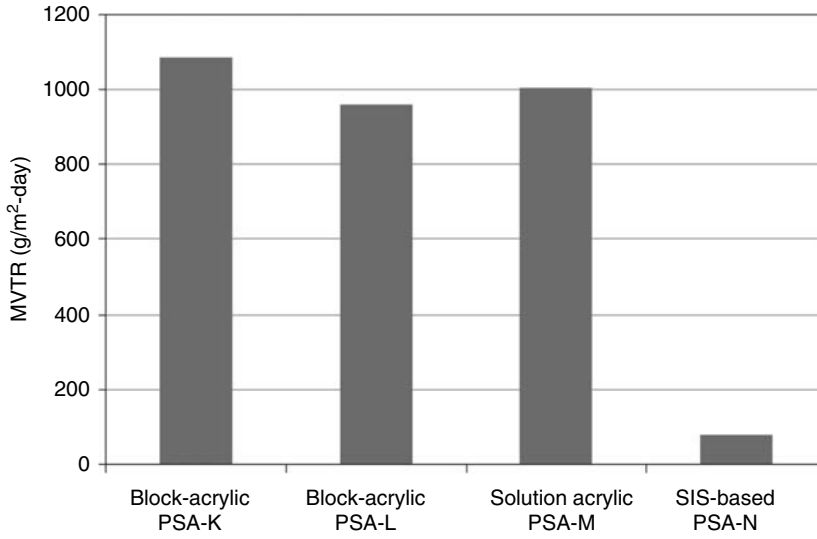


FIGURE 3.21 Moisture vapor transmission rate using the inverted cup method (adhesive films were 0.038 mm thick and backed with a porous film).

TABLE 3.15 Model Formulation and Performance of AHMPSA for Medical Application

Formulation	Parts (%) by Weight
ABCP1	31
Arakawa KE-100	45
Poly G 26-150	27
Test	Performance
Viscosity @ 163°C	18.6 Pa · s
180° peel off SS (N/m)	245.2
Loop tack on SS (g/cm^2)	127.4
Shear, 15 KPa (SS) (h)	67

adhesives (PSA-K and PSA-L) with a solution acrylic medical adhesive (PSA-M) and a SIS-based medical grade (PSA-N). The AHM adhesives and solution acrylic adhesive have similar MVTR values between 950 and 1100 ($g/m^2 \cdot day$) and all three are much higher than that of the SIS-based adhesive, which is below 100($g/m^2 \cdot day$). A skin wear study performed by a panel of volunteers also confirmed the superior 24-h adhesion from the AHM-based medical adhesives compared with the SIS-based adhesives [66]. In addition, both AHM adhesives, PSA-K and PSA-L, as well as the MAM block copolymers passed the cytotoxicity test using the ISO elution method (International Organization for Standardization Method 10993, part 5) [66]. An example of a typical formulation and performance of MAM triblock copolymer-based medical adhesive is presented in Table 3.15 [71]. ABCP1 is a commercial grade of MAM block copolymer by Kuraray; KE-100 (SP = 95°C) is a disproportionated and hydrogenated rosin ester supplied by Arakawa Chemical Industries, Co., Osaka, Japan and Poly G®26–150 is available from Arch Chemicals, Inc., Norwalk, CT.

For graphic applications, despite the promise of excellent clarity and UV stability from MAM block copolymers, improper tackifier used in the formula may still cause degradation and discoloration. One of the key considerations in designing a graphic grade of AHMPSA is to select hydrogenated and colorless tackifiers to maintain the clarity and color stability of the final adhesives.

Removable applications are another potential area in which to utilize acrylic hot melts. A good removable PSA requires low peel force with clean removal and, more importantly, little to no peel build-up over a period of time under elevated temperatures and various humidity conditions. Traditional removable PSA grades are made by cross-linked solution acrylics (see also *Applications of Pressure-Sensitive Products*, Chapter 8). However, a one-part, self-cross-linked mechanism does not completely get rid of the low-molecular-weight species and is thus not sufficient to prevent further wet-out and peel build-up. Therefore, a two-part system is often used to achieve high cross-linking density. The downside of the two-part adhesive is the short pot life, as well as difficulties in handling and processing (see also Chapter 8). A possible solution is to use acrylic block copolymers to develop new removable grades. Because the MAM polymer is polymerized through living anionic synthesis, it has very uniform molecular weight and very narrow polydispersity. There are no low-molecular-weight oligomers

TABLE 3.16 Removable AHM PSA Performance

Test (on SS substrate)	Performance
Viscosity @ 163°C	4.8 Pa · s
180° peel, 20-min at room temperature (RT) (N/m)	131.3
180° peel, 24-h at RT (N/m)	109.5
180° peel, 7 days at RT (N/m)	142.3
180° peel, 7 days at 35°C/95% relative humidity (N/m)	120.4
180° peel, 7 days at 65°C (N/m)	262.7
Loop tack (g/cm^2)	87.9
Shear, 30 KPa (h)	3

or residual monomers present in the system. The instant wet-out characteristic of the AHMPSAs significantly minimizes the peel build-up. The stable nature of the acrylic block copolymer, as well as its high heat resistance, helps AHMs to maintain the initial peel resistance and cohesive strength at various temperature conditions. Through careful design and formulation, the AHMPSAs can have a long modulus plateau over a wide frequency range, which ensures similar peel resistance and failure mode at various removal rates. In addition, the fact that AHM adhesives tend to have low stretchability and low overall work of adhesion make them easier for clean removal and low peel resistance to various substrates. It is also important to point out that, due to dilution from tackifiers and plasticizers, it is not a trivial effort to control migration and bleeding in a removable AHM. Table 3.16 provides an example of the performance of a prototype MAM triblock copolymer-based removable PSA. Minimum peel build up is achieved under various aging conditions.

As an emerging technology, ABC-based HMPSAs are growing rapidly and have caught market attention. The continuing drive to develop new generations of ABCs and new AHM tailored tackifiers will accelerate commercial growth.

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4

Polyisobutene-Based Pressure-Sensitive Adhesives

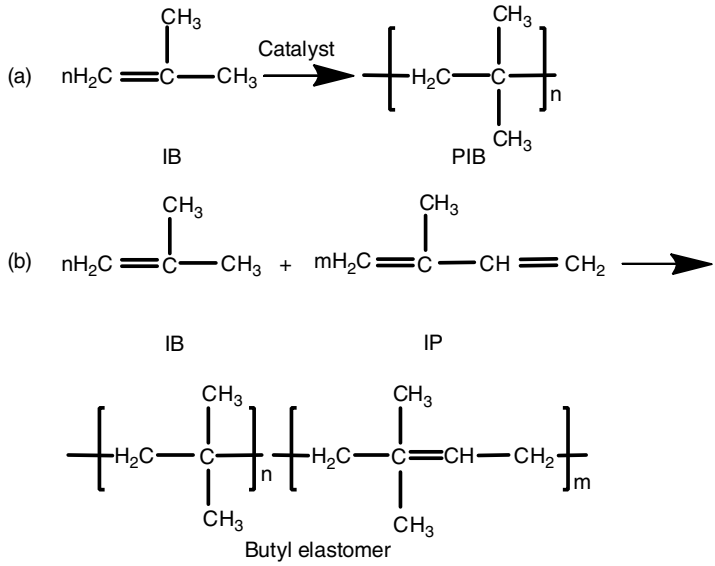
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4.1 Polyisobutene (PIB): General Properties and Applications

PIB is a vinyl polymer that is made from the monomer isobutylene (IB) by cationic polymerization (Scheme 4.1a).

Despite its linear structure, PIB is usually classified as a synthetic rubber or elastomer. PIB has unique properties: very low air, moisture, and gas permeability, good thermal and oxidative stability, chemical resistance, and high tack in adhesive formulations. PIB is a colorless to light-yellow, elastic, semisolid or viscous substance. It is odorless, tasteless, and nontoxic. Because of their highly paraffinic and nonpolar nature, PIBs are soluble in aliphatic and aromatic hydrocarbon solvents and insoluble in polar solvents. Solubility generally decreases with increasing molecular weight of the polymer and increasing size of the aliphatic portion of the solvent molecule. The amorphous characteristics and low glass transition temperature ($T_g = -62°C$) of PIB impart high flexibility and permanent tack. Despite the favorable tack property, the adhesion of PIBs to many surfaces is weak because of their low polarity. This problem can be overcome by the addition of tackifiers (such as rosin ester resins) and other materials that will impart some polar properties to the formulation (see also *Technology of Pressure-Sensitive Adhesives and Products*, Chapter 8).



SCHEME 4.1 Polymerization of isobutylene (IB) to form polyisobutylene (PIB) (a); copolimerization with isoprene (IP) to form butyl elastomer (b).

TABLE 4.1 Physical Properties of PIB That are Independent of Molecular Weight

Density at 20°C	0.92 g/cm
Glass transition temperature, T_g (differential scanning calorimetry)	−62°C
Specific heat, c	2 kJ·kg^{-1}·K^{-1}
Thermal coefficient of cubic expansion at 23°C	6.3 × 10^{-4} K^{-1}
Thermal conductivity, k	0.19 W·K^{-1}·m^{-1}
Refractive index, n^{20}D	1.51
Dielectric constant, ε_r (50 Hz, 23°C)	2.2
Dissipation factor, $tg\ \delta$ (50 Hz, 23°C)	≤5 × 10^{-4}
Specific resistance	1.016 Ω·cm
Coefficient of permeability to water vapor	2.5 × 10^{-7} g·m^{-1}·h^{-1}·mbar^{-1}

PIB is used in making adhesives, agricultural chemicals, fiber optic compounds, caulks and sealants, cling film, electrical fluids, lubricants (two-cycle engine oil), paper and pulp, personal care products, and pigment concentrates, for rubber and polymer modification, as a gasoline/diesel fuel additive, and even in chewing gum. Low- and medium-molecular-weight PIBs are used as viscosity modifiers, fuel and lubricating oil additives, tack improvers in adhesive formulations, and primary binders in caulking and sealing compounds. The most important physical properties of PIB are presented in Table 4.1.

PIBs are usually classified into two groups according to molecular weight. High-molecular-weight PIBs have a weight average molecular weight, M_w, of from 500,000 to 1,100,000 g/mol, preferably between 650,000 and 850,000 g/mol. Such polymers are available commercially, for example, under the trade name Oppanol® B80-B200, B30

SF–B50 SF (BASF AG, Ludwigshafen, Germany) or Vistanex® MM-L80 through L-140 (ExxonMobil Chemical Company, Houston, TX) [1–3].

Low- and medium-molecular-weight PIBs have a weight average molecular weight, M_w, of from 40,000 to 120,000 g/mol, preferably between 60,000 and 100,000 g/mol. Such polymers are available commercially, for example, under the trade name Oppanol B10 SFN-B15 SFN (BASF AG) or Vistanex LM-MH, LM-MS, and LM-H (ExxonMobil Chemical Company) [3,4].

The discovery of the low permeability of PIB led to the development of butyl rubber (BR). Butyl elastomer is a random copolymer of IB and 1–4 mol % of isoprene (IP) (Scheme 4.1b). Double bonds introduced into the macromolecule by isoprene permit the polymer to be cross-linked or vulcanized. The physical properties of BR are mostly the same as those of PIB: low permeability, good chemical and thermal stability due to the low unsaturation content, and high damping. BR is cross-linked (cured or vulcanized) with sulfur-based chemistry and mostly used as an inner liner or tube in tires to prevent air leakage. Other applications include tank liners, vibration dampers, protective clothing, tire curing bladders, railway pads, wire and cable coating, belting, and hoses. Cross-linked BR is also used for pharmaceutical stoppers and blood bags because of its excellent barrier properties. Both PIB and non-cross-linked butyl elastomers are approved by the Food and Drug Administration as a chewing-gum base and for other food-related applications (see also *Applications of Pressure-Sensitive Products*, Chapter 7). BR is used for PSAs as well (see also *Technology of Pressure-Sensitive Adhesives and Products*, Chapter 8).

BRs are available both in nonhalogenated and in several halogenated grades. A low-molecular-weight, semiliquid analog of BR is also available under the trademark Kalene® (Hardmann, Inc., Belleville, NJ). Kalene liquid BRs impart the performance benefits of BR and provide the processing convenience of a liquid. Kalene's butyl properties impart chemical resistance to a wide variety of sealants and adhesives. Kalene products provide tack to PSAs and they improve the adhesion of butyl-based adhesives and sealants. They also act as reactive plasticizers for conventional butyl to improve their compounding efficiency.

The halogenation of BR, with either chlorine or bromine, significantly increases cure reactivity, provides compatibility with unsaturated polymers, and enhances adhesion compared with regular BR. Significant improvements in heat, ozone, flex fatigue resistance, and compression set can be achieved through the selection of appropriate compounding ingredients and curing systems. Chloro-BR is prepared by chlorinating the regular butyl polymer under controlled conditions so that the reaction is primarily by substitution and little of the unsaturation originally present in the macromolecules is lost. ChloroBR consists of approximately 1.2 wt % chlorine, which tends to enhance the reactivity of the double bonds as well as supply additional reactive sites for cross-linking. Brominated butyl polymers are also available. They are similar to chlorobutyl, but provide an additional level of cross-linking activity. Bromo-BR consists of approximately 20 wt % bromine.

A relatively new family of butyl elastomers are star-branched (SB) butyl polymers, both nonhalogenated and halogenated. These polymers have a unique molecular weight distribution due to incorporating large SB molecules with butyl arms. SB butyl polymers have functional properties of butyl and halobutyl polymers. However, because of their unique

TABLE 4.2 Commercial Grades of PIBs

Name	Grade	Viscosity Average Molecular Weight (M_v/g/mol)	Comments
BASF Oppanol B	10 SNF	40,000	Soft, resin-like polymers, used in the production of adhesives, sealants, lubricants, coatings, and chewing gum
	11 SNF	49,000	
	12 SNF	55,000	
	13 SNF	65,000	
	15 SNF	85,000	
	30 SF	200,000	Soft, resin-like polymers, used for producing adhesives, sealants, lubricating oils, coating compounds, and chewing gum; also recommended for modifying bitumen
	50/50 SF	400,000	
	80	800,000	
	100	1,100,000	Rubbery polymers, used for the production of adhesives, sealants, lubricants, and coating compounds
	150	2,600,000	
	200	4,000,000	
Exxon Vistanex	LM-MS	44,000	Semiliquid polymers, used mainly as permanent tackifiers in a variety of cements, PSAs, and hot-melt adhesives; useful for enchancing adhesion to polyolefin surfaces
	LM-MH	53,000	
	LM-H	63,000	
	MM L-80	900,000	Rubber-like solids used to impart strength and flow resistance to solvent cement and PSA label stock; also used in certain hot-melt adhesion compositions where they provide flexibility and impact resistance, particularly at low temperature
	MM L-100	1,250,000	
	MM L-120	1,660,000	
	MM L-140	2,110,000	
Kalene liquid BR	800	36,000	Used as bases for sealants, coatings, and adhesives
	1300	42,000	
Exxon butyl	007	450,000	Used in products needing low permeability to gases and liquids, e.g., tire inner liners, hoses, seals of certain types, and membranes; also suitable for curing bags, pharmaceutical stoppers, and rubber articles needing good resistance to chemicals, weathering, and ozone, such as tank linings, conveyor belts, and protective clothing
	065	330,000	
	068	450,000	
	165	330,000	
	268	480,000	
	269	520,000	
	365	330,000	
Lanxess butyl	101-3		
	301		
	402		
Exxon chlorobutyl	1066	400.000	Chlorobutyl can be blended with both regular butyl and natural rubber and then preferentially cured through chlorine to improve strength; the reactive chlorine increases adhesion to many polar substrates
	1068	480.000	
Lanxess chlorobutyl	1240		
Exxon bromobutyl	2211		Used for the production of tires, particularly tire inner liners and tire sidewalls, and for pharmaceutical rubber articles
	2222	330,000	
	2235	420,000	
	2244	450,000	
	2255	450,000	

(*continued*)

TABLE 4.2 (Continued)

Name	Grade	Viscosity Average Molecular Weight (M_v/g/mol)	Comments
Lanxess bromobutyl	2030 2040 X2		
Exxon SB butyl	4266 4268	All grades are bimodal and contain approximately 13–14 wt % high-molecular weight star fraction	Used in pharmaceutical closures, etc.
Exxon SB chlorobutyl	5066		
Exxon SB bromobutyl	6222 6255		
Exxpro speciality elastomer	3035 3433 3745	430,000 350,000	Used when extended age resistance at high temperature is needed
Lord BR latex	BL-100		Used in packaging adhesive applications and as a tackifying and flexibilizing additive in higher strength adhesives based on more brittle polymers

molecular weight distribution, they offer improvements in green strength (uncured strength)/stress relaxation balance and melt rheology. This leads to potential benefits in reduced cold flow, better extrudate/calendered surface quality, and enhanced mixing.

Exxpro elastomers are new elastomers that are randomly brominated copolymers of *para*-methylstyrene (PMS) and isobutylene with varying degrees of PMS content and bromination on the *para*-methyl group. These elastomers retain all the properties of butyl and halobutyl, but the inertness of the backbone improves heat, ozone, and flex resistance.

BR can be also emulsified to give a latex. The advantage of latex is high (approximately 60 wt %) solid content and low viscosity. Butyl latex has excellent mechanical, chemical, and freeze–thaw stability, which allows compounding and blending with other ingredients. When dried, it possesses the typical butyl characteristics of low aging, flexibility, low permeability, and tack.

Commercial grades of PIBs and BRs are listed in Table 4.2.

4.2 Polyisobutene-Based Pressure-Sensitive Adhesives

PIB has long been used as a basic substance in the compounding of pressure-sensitive adhesives (PSAs). Relative to other known elastomers, synthetic polymers based on isobutylene offer a number of advantages. Owing to their synthetic production, they are free of unwanted ingredients and due to their complete saturation they are highly stable to oxidation. PIBs are not a skin irritant and adhesives used in medicine (e.g., surgical tape adhesive, transdermal systems) [5] are usually based on PIBs (see also *Applications of Pressure-Sensitive Products*, Chapter 4). PIBs are used in many adhesive formulations

due to their tackiness, flexibility, and low cohesive strength, mainly in PSAs and hot-melt adhesives.

PSAs for removable labels and tapes are usually formulated as blends of rubber and tackifying resins (see also *Technology of Pressure-Sensitive Adhesives and Products*, Chapter 8). High-molecular-weight PIBs are strong and elastic and can serve as the elastomeric base of PSAs [1,2]. Low-molecular-weight PIBs are very soft and liquid-like, making them suitable tackifiers [4]. Tack and holding power are two important parameters for PSAs (see also *Fundamentals of Pressure Sensitivity*, Chapters 6 and 8, and *Applications of Pressure-Sensitive Products*, Chapter 7). Tack of PIB-based PSAs can also be adjusted with different resins and other tackifiers. The cohesive strength of PIBs is relatively low, but can be increased by the addition of high-molecular-weight PIB or fillers. PSAs formulated with PIB are aging-resistant and used for adhesion to a variety of substrates [e.g., glass, metal, paper, polyvinyl chloride (PVC) and polyester films].

PIBs can also be formulated in hot-melt PSA (HMPSA) recipes. PIBs improve the flexibility of the system, provide good aging and chemical resistance, and increase tack. However, high-molecular-weight grades of PIB increase melt viscosity and, therefore, they are usually blended with a significant amount of tackifying resin, petrolatum, or amorphous polypropylene to reduce viscosity to an appropriate level.

It should also be noted that PIB-based PSAs are widely used in the medical field [5,6], especially for transdermal drug delivery (TDD) systems [7–12] (see also *Applications of Pressure-Sensitive Products*, Chapter 4). TDD systems are drug-loaded adhesive patches that, when applied to the skin, deliver the therapeutic agent, at a controlled rate, through the skin to the systemic circulation and the target organs [9]. In TDD applications, adhesives are used to maintain intimate contact between the patch and the skin surface. The manufacturers of PIB polymers do not supply preformulated, ready-to-use adhesives; therefore, the TDD patch manufacturers or formulators usually compound their own PIB–PSA recipes.

There are three common approaches to obtain desired PSA properties. First, a combination of low- and high-molecular-weight PIBs is used to achieve a balance of tack and cohesive strength. Such adhesives can be easily manufactured by solution or dry blending and a certain ratio of low- to high-molecular-weight PIB is required for pressure-sensitive adhesion. Conventionally, this is accepted to be about 80 wt % or less of low-molecular-weight PIB. This sort of formulation yields PSAs with fairly mild adhesive characteristics. Second, high- and medium-molecular-weight PIBs are blended with a low-molecular-weight polybutene (PB). When PB is added to the PIB mixture, the formulation range expands. One can use higher ratios of high- to low-molecular-weight PIB. The formulation then becomes a compromise between highly tacky material (high amount of PB) and materials with low shear strength. Third, tackifiers, plasticizers, fillers, waxes, oils, and other additives can be incorporated into the formulation to impart the desired adhesive properties and viscosity. Fully formulated PIB adhesives for TDD applications are available from Adhesives Research, Inc. (Glen Rock, PA) and custom formulations can be provided by other vendors such as Mactac (Moosic, PA) and National Starch and Chemical Company (Bridgewater, NJ) [9].

Several typical PSA formulations illustrating some of the application, as well as their suppliers, are listed in Table 4.3 and can also be found in handbooks and patent literature [13–23].

TABLE 4.3 PSA Formulations

Component	Supplier	Content
A. Pressure-Sensitive Adhesive [3]		
Vistanex PIB MM L-120	Exxon Chemical Co.	100 parts
Hercolyn	Hercules, Inc.	30 parts
Piccolyte S115	Hercules, Inc.	45 parts
Parapol 950	Exxon Chemical Co.	70 parts
B. BR HMPSA [13]		
Exxon butyl 065	Exxon Chemical Co.	100 parts
Ercorez 5320 resin	Exxon Chemical Co.	10 parts
Petrolatum		50 parts
Amber mirowax (Be Square 175)	Petrolite Corp., Polymer Div.	150 parts
Antioxidant (Ethanox 702 or Irganox 1010)	Albemarle Corp.	1 part
C. High Heat-Resistant PSA [13]		
Exxpro elastomer	Exxon Chemical Co.	100 parts
Ercorez 2550 resin	Exxon Chemical Co.	110 parts
Ercorez 5380 resin	Exxon Chemical Co.	15 parts
Cross-linker (e.g., triethylene tetramine)		0.5 parts
Antioxidant		2 parts
D. Monolith Adhesive Transdermal System [17]		
PIB Oppanol B1	BASF	5 g
PIB Oppanol B10	BASF	3 g
PIB Oppanol B100	BASF	9 g
Hydrogenated carbon resin Ercorez 5320	Exxon Chemical Co.	43 g
1-dodecylazacycloheptan-2-one	Azone, Nelson Res., Irvine, CA	20 g
Active ingredient (3-amino-1-hydroxypropane-1,1-diphosphonic acid)		20 g
E. Adhesive Material for Skin [15]		
Vistanex PIB LM-MH	Exxon Chemical Co.	41.5%
Kraton D1107 (Styrene–isoprene–styrene copolymer)		8.5%
Gelatine P.S.98.240.223	Ed. Geistlich Söhne AG	17.5%
Pectine LM12 CG Z or USP/100	Copenhagen Pectin A/S	10%
CMC (carboxylmethylcellulose) AF2881	Akzo	22.5%

4.3 Rheology, Viscoelasticity, and Adhesion of Polyisobutylene-Based Pressure-Sensitive Adhesives

PIB is a linear polymer with a moderate width of molecular weight distribution. Typically, the ratio of weight-to-number average molecular weight, M_w/M_n, is around 2. The rheological properties of such polymers are essentially controlled by M_w and temperature, T. Low-molecular-weight grades ($M_w < 10^4$ g/mol) exhibit newtonian flow behavior

at room temperature and above and in this case the viscosity, η, is directly proportional to M_w.

Higher-molecular-weight PIBs are shear thinning and the dependence of viscosity, η, on shear rate, $\dot{\gamma}$, is well described by the Cross model [24].

$$\eta(\dot{\gamma}) = \frac{\eta_0}{1 + |\lambda\dot{\gamma}|^{0.75}} \tag{4.1}$$

Here, λ is a characteristic time constant depending on molecular weight and temperature (and pressure), whereas η_0 is the viscosity in the limit of low shear rates, the so-called zero-shear viscosity. The molecular weight dependence of this important quantity has been investigated intensively [25–28]. The following relationship between η_0 and M_w has been extracted from a large set of experimental data [28].

$$\eta_0 = 4.69 \cdot 10^{-12} \cdot M_w^{3.43} \cdot Pa \cdot s \tag{4.2}$$

This relation is valid for $T = 25°C$. The temperature dependence of η_0 is described by the William–Landel–Ferry (WLF) equation and can be expressed in terms of a shift factor a_T,

$$\log a_T = \log\left(\frac{\eta_0(T)}{\eta_0(T_0)}\right) = -\frac{c_1(T - T_0)}{c_2 + (T - T_0)} \tag{4.3}$$

with $T_0 = 25°C$, $c_1 = 8.61$, and $c_2 = 200$ K [27], which is consistent with other literature data [28,29] referring to other reference temperatures, T_0.

At temperatures well above T_g, the WLF equation can also be approximated by an Arrhenius equation with a single activation energy parameter, E_a. The linear viscoelastic properties of polymers are usually described in terms of a complex frequency-dependent shear modulus $G^*(\omega) = G' + iG''$, where the storage modulus, G', characterizes the elastic and the loss modulus, G'', characterizes the viscous contribution to stress relaxation (see also *Technology of Pressure-Sensitive Adhesives and Products*, Chapter 5, *Fundamentals of Pressure Sensitivity*, Chapter 5, and *Applications of Pressure-Sensitive Products*, Chapter 7). A typical result for PIB (Oppanol B50, $M_v = 400{,}000$ g/mol) is illustrated in Figure 4.1. These G' and G'' curves demonstrated two characteristic crossover frequencies ($G' = G''$), ω_c and ω_e, which separate the spectra into three parts. At frequencies below ω_c, in the so-called flow regime or terminal zone, G'' dominates over G' and $G' \sim \omega^2$, whereas $G'' \sim \omega$. In the intermediate so-called entanglement or rubbery regime, $G' = G_0$ is essentially independent of frequency and $G' >> G''$. This is a consequence of the topological constraints the polymer chains impose on each other. This phenomenon is also called entanglement and the entanglements are like physical, nonpermanent cross-links, which control stress relaxation. The corresponding plateau modulus $G_0 = \rho RT/M_e$ is directly related to the average molecular weight between two entanglements, M_e. This constant is a material property independent of molecular weight and for PIB $M_e = 8{,}700$ g/mol [30]. In the glass transition zone both G' and G'' exhibit power-law behavior and finally, at high enough frequencies, the shear modulus G_s of the solid material is reached.

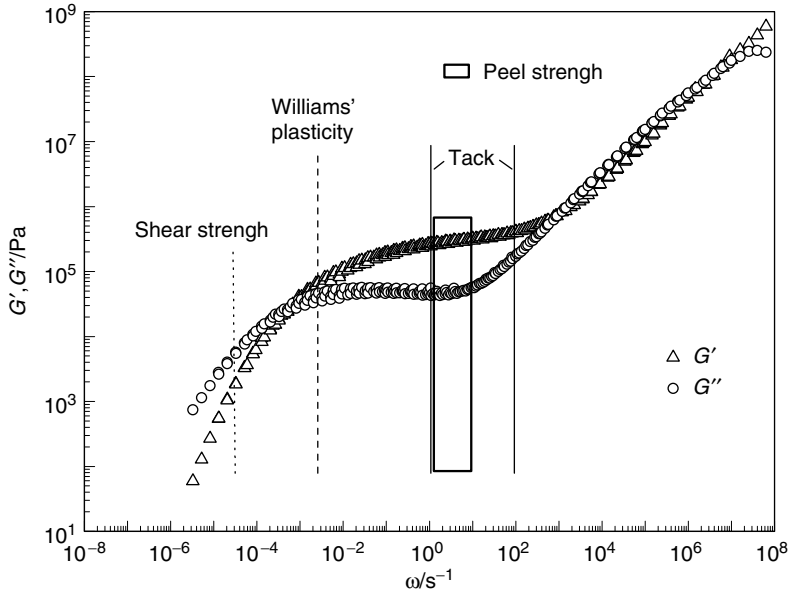


FIGURE 4.1 G', G'' vsersus ω for Oppanol B50. Master curve for $T = 25°C$. (Modified from Zosel, A., *J. Adhesion.*, 44, 6, 1994.)

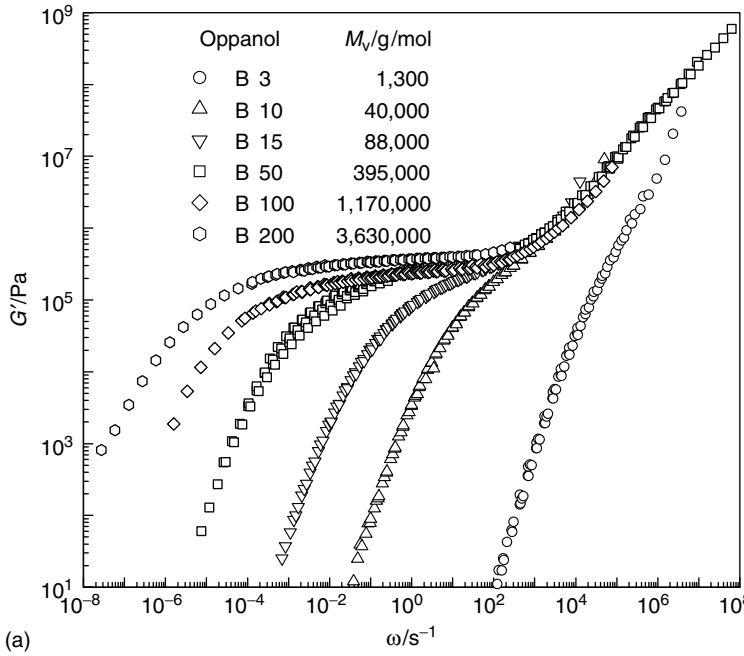
The viscoelastic properties in the glass transition regime, as well as ω_e and G_0, are independent of molecular weight. In contrast, ω_c^{-1} scales with $M_w^{3.4}$ similar to η_0; as a consequence, the entanglement regime gets broader with increasing molecular weight and the terminal zone is shifted to lower frequencies. This is demonstrated for different grades of Oppanol B in Figure 4.2. Finally, it should be noted that the Cox–Merz rule is valid for PIB and the steady shear viscosity η (γ̇) can be calculated from G' and G'' according to [31].

$$\eta(\dot{\gamma}) = |\eta^*|(\omega) = \frac{1}{\omega}\sqrt{G'^2 + G''^2} \quad \text{for} \quad \omega = \dot{\gamma} \tag{4.4}$$

Frequently, the molecular weight of PIB is determined from viscosity measurements of dilute solutions. This method yields the viscosity-average molecular weight, M_v, often provided in data sheets. The zero-shear viscosity of the corresponding melt can be calculated from the intrinsic viscosity [η] determined from dilute solution viscometry. For solutions of PIB in cyclohexane at $T_0 = 25°C$, the following relation holds [28].

$$\eta_0 = 4.27 \cdot 10^6 \cdot [\eta]^{4.66} \tag{4.5}$$

The adhesive properties of PIB such as tack, shear, or peel resistance are closely related to its viscoelastic and rheological properties outlined above. A rough empirical correlation between relevant shear moduli G' and G'' and different adhesion tests is provided in Figure 4.1. The static shear strength often characterized by a characteristic holding time, t_c, can also be correlated to the steady shear viscosity η at $\dot{\gamma} = 0.1\ s^{-1}$ [32].



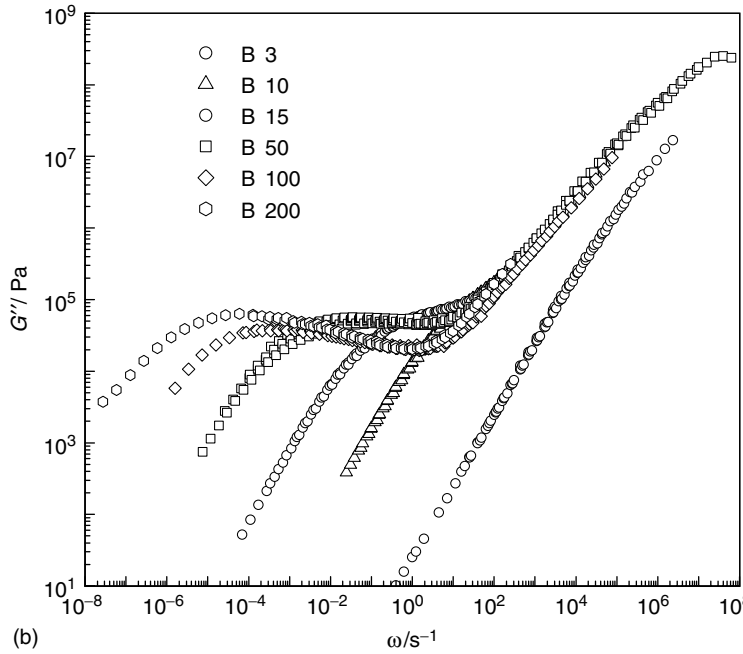


FIGURE 4.2 G' (a) and G'' (b) versus ω for various Oppanol grades.

Zosel [33] calculated the full time dependence of the shear deformation $\Delta l/l_0$, as well as t_c, from $\eta(\dot{\gamma})$ using approximations from linear viscoelasticity and found good agreement with experimental results for materials with low to moderate viscosities, but a significant overestimation of these quantities for high-viscosity PIB ($M_v = 380{,}000$ g/mol).

The resistance to shear increases strongly with molecular weight up to $M_w \approx 10^6$ g/mol and then decreases, accompanied by a transition from cohesive to adhesive failure [32]. Shear resistance can be significantly improved by blending low-molecular-weight species with small amounts of high-molecular-weight grades without a significant change in viscosity.

Peel resistance is another important adhesive property that is closely related to viscoelasticity [34]. Irrespective of test conditions, low-molecular-weight, low-viscosity PIBs exhibit a higher peel resistance than higher-molecular-weight species due to better wetting of the substrate. The transition from cohesive to adhesive failure occurs at room temperature around $M_w = 40{,}000$ g/mol [32]. The deformation of an adhesive across the peel front is mainly extensional [35,36]. Accordingly, Christensen and colleagues [37,38] determined the transient extensional viscosity of PIB mixtures at different strain rates. In combination with appropriate constitutive equations accounting for strain hardening and knowledge of the true shape of the peel front, they were able to establish a model predicting peel force from peel rate, quantitatively.

The peel resistance of PIB on steel can be significantly increased by oxygen plasma treatment of the adhesive, which results in an increase of the carbonyl group concentration in a thin layer (≈100 nm) adjacent to the substrate [39].

Tack is another important criterion for judging adhesive properties of PSAs. Tack is determined by bond formation, as well as bond separation, and hence depends on numerous experimental factors like contact time and force, chemical nature, and roughness of the substrate or debonding rate, but also on PSA properties like viscosity, viscoelasticity, and surface tension. A general review of tack, including a detailed discussion of these aspects, can be found in Ref. [40] (see also *Fundamentals of Pressure Sensitivity*, Chapter 6). Here, we focus on PIB-related tack experiments and their essential results. Tack is characterized by the fracture energy, G_A (often also termed work of adhesion, W_{adh}), which is defined as

$$G_A = \frac{1}{A}\int_0^{t_B} F \cdot \upsilon dt = d\int_0^{\varepsilon_B} \sigma \cdot d\varepsilon \tag{4.6}$$

where A is the contact area, F is the force during debonding, υ is debonding rate, t_B is the time of failure, d is the thickness of the adhesive layer, and ε_B is the deformation at failure.

For PIB, as well as for many other polymers, G_A increases with increasing contact time and force. This is especially pronounced on rough substrates for low contact time and force [41]. Furthermore, G_A can be related to the time-dependent stress relaxation modulus $G(t)$, taking into account the true contact area of a rough substrate as a function of contact time and force [42].

In general, bond formation/wetting increases, whereas cohesive and adhesive strength decrease with increasing temperature. Therefore, the fracture energy in a tack experiment is supposed to go through a maximum as a function of temperature. For PIB this

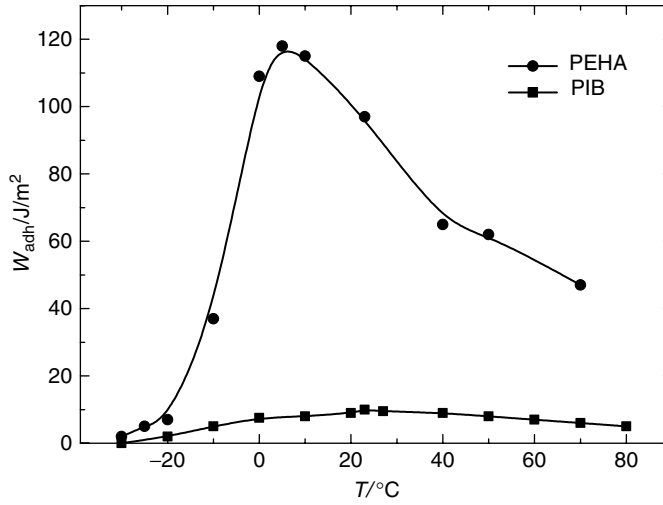


FIGURE 4.3 Adhesive energy, W_{adh}, as a function of temperature for polyethylhexyl acrylate (PEHA) and PIB. (Modified from Zosel, A., *J. Adhesion.*, 30, 143, 1989.)

maximum occurs around room temperature (Figure 4.3) [43]. The fracture energy, G_A, is related to the plateau modulus, G_0, and, according to Dahlquist's criterion [44], a good PSA should have a $G_0 < 3 \times 10^5$ Pa. For PIB $G_0 \approx 3 \times 10^5$ Pa due to its low M_e and, accordingly, pure PIB does not exhibit tack properties typical for PSAs. The debonding process of PSAs in a tack experiment is controlled by cavitation and fibrillation. Cavitation determines the maximum stress occurring during this process, whereas fibrillation results in a subsequent extended stress plateau and usually controls the maximum strain at which failure occurs.

Owing to its dense entanglement network (low M_e), PIB does not form fibrils and the stress versus strain curves during debonding exhibit a sharp maximum but no plateau in the temperature range from −10°C to +60°C, as illustrated in Figure 4.4. This is termed "brittle" failure [45]. Accordingly, the fracture energy is much lower for PIB than for typical acrylate PSAs, as illustrated, for example, in Figure 4.3. Nevertheless, high-molecular-weight PIB grades can serve as a valuable elastomeric basis for PSA formulations, whereas low-molecular-weight grades ($M_v < M_e$) are liquid-like, suitable tackifiers. In the molecular weight range $M_v \geq 50{,}000$ g/mol, the fracture energy [30], as well as the peak stress [32] during debonding, rapidly decay with increasing M_v. This can be attributed [30,32] to the drastic increase in viscosity ($\sim M_w^{3.4}$), which progressively aggravates wetting of the substrate.

PIB can be easily blended with resins, solvents, or other low-molecular-weight components. Thus, the entanglement density can be reduced drastically. As a consequence, the plateau modulus, G_0, decreases (and M_e increases), Dahlquist's criterion is fulfilled, and such mixtures clearly exhibit both cavitation and fibrillation during debonding in tack experiments. This is illustrated in Figure 4.5 [46] for an 80/20 blend of high-molecular-weight PIB ($M_v = 6{,}650{,}000$ g/mol) with another grade with $M_v = 1{,}500$ g/mol (well below M_e).

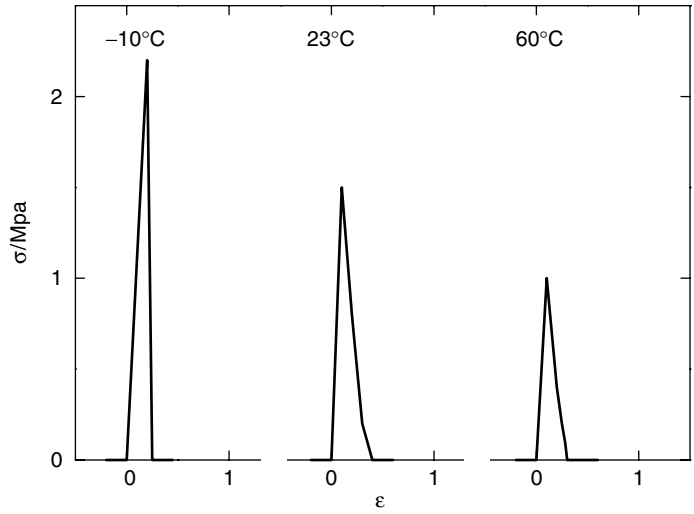


FIGURE 4.4 Probe tack stress–strain curves for PIB during bond separation at various temperatures. (Modified from Zosel, A., *J. Adhesion*, 30, 144, 1989.)

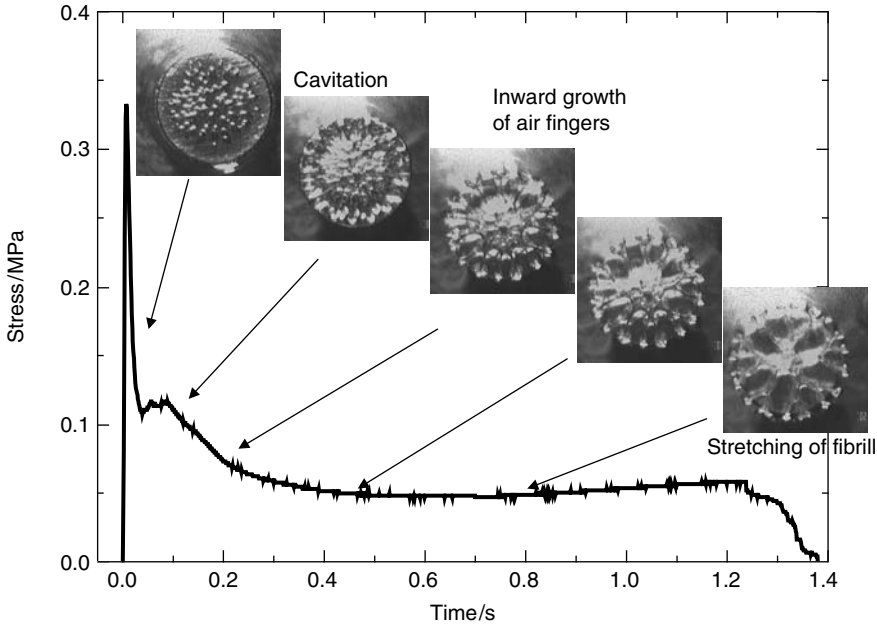


FIGURE 4.5 Cavitation and fibrillation related to characteristic probe tack debonding curve of an 80/20 blend of B1/B6650 at 25°C, F_c = 5N, dwell-time t_d = 1 s, debonding rate v = 1 mm/s. (Modified from O'Connor, A. E., and Willenbacher, N., *Int. J. Adhesion Adhesives*, 24, 338, 2004.)

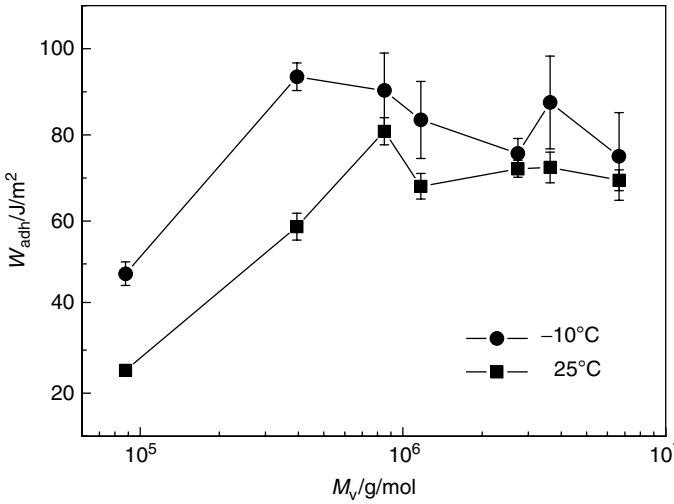


FIGURE 4.6 Adhesive energy, W_{adh}, for the 80/20 blends Bl/BX for samples BX with different M_v at $T = 25°C$ and $-10°C$. Test conditions: $F_c = 2N$, dwell-time $t_d = 1$ s, debonding rate $v = 1$ mm/s. (Adapted from O'Connor, A. E., and Willenbacher, N., *Int. J. Adhesion Adhesives*, 24, 341, 2004.)

Even if Dahlquist's criterion is fulfilled, a minimum molecular weight or number of entanglements per polymer chain is required for fibrillation. As long as the molecular weight is below this threshold, the fracture energy strongly increases but then essentially levels off at higher molecular weight (Figure 4.6).

As previously mentioned, wetting of a substrate by the adhesive is another important parameter controlling tack. In addition to surface roughness and adhesive viscosity, interfacial tension has a strong impact on this phenomenon (see also *Fundamentals of Pressure Sensitivity*, Chapter 1). The surface tension of PIB is 33 mN/m and high tack values are reached if the surface tension of the adherent is close to or higher than this value [43].

The adhesive properties of PIB with a carboxymethylcellulose (CMC) filler have also been investigated [47,48]. Such a composition is widely used as a main component of PSAs suitable for contact with the human body because, apart from the excellent adhesion and physiological neutrality, it is capable of absorbing moisture. Tack and peel resistance have been measured in combination with different substrates and at different bonding/debonding conditions. Cohesive strength is lowered by the presence of the inert CMC component and peel resistance decreases with increasing CMC content, with the exception of high peel rates, where adhesive failure dominates.

A pronounced maximum of the time or strain of failure in tack experiments was determined at a CMC content of about 35%. This again corresponds to the viscoelastic properties of the adhesive, because at this PIB/CMC ratio the plateau modulus, G_0, decreases below Dahlquist's criterion and allows for substantial fibrillation during debonding.

4.4 Conclusions

PIB and the corresponding BRs provide unique properties such as very low moisture and gas permeability, high chemical resistance, and thermal stability; they are odorless, tasteless, and nontoxic and are therefore used in a wide variety of different sealant and adhesive applications. PIB is a linear polymer with a relatively narrow molecular weight distribution. Its amorphous structure and low T_g result in a high permanent flexibility. Various grades covering a broad range of average molecular weight from several thousand to more than 1,000,000 g/mol are commercially available. Systematic research using this broad range of different PIB grades has provided valuable insight into the relationship between viscoelastic and adhesives properties of soft polymers in general and has thus promoted the whole field of research and development of PSAs. More importantly, the availability of these different molecular weight grades offers the advantage of easily tailoring adhesive and cohesive PSA properties, especially in combination with other elastomers, tackifiers, or fillers, to achieve the desired application properties. High-molecular-weight grades serve as a valuable elastomeric basis for PSA formulations; they exhibit a high cohesive strength and demonstrate brittle failure in tack experiments due to the low entanglement molecular weight, M_e. Low-molecular-weight grades are liquid-like, suitable tackifiers and promote wetting and adhesion. PIB is widely used in well-established application areas like building and construction or packaging and tapes. Owing to its nontoxicity, it is approved for food/food contact and thus is of special interest for food packaging. Its stability, damping, and sealing properties make it an interesting material for well-established as well as upcoming automotive applications. Along with the growing market for HMPSAs, PIB will be of increasing relevance. Medical PSA applications will grow, new applications in this area will come up, and, due to its non-skin-irritating and nontoxic features, PIB will be of particular importance in this field.

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5

Acrylic Adhesives

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5.1 Introduction

The first use of acrylic acid esters as pressure-sensitive adhesives (PSAs) is generally attributed to Walter Bauer working at the Röhm and Haas Company in 1928 [1]. His polymers, used to bond paper, glass, or material to metals and described simply as an adhesive, were applied either as a 10% solution in acetone or as a film placed between the adherends. *"Durch Anwendung von Druck und Wärme wird dann gute Verklebung erzielt"*; translation: *"A good bond is created by the application of pressure and heat."* How much pressure and heat was not disclosed and it was not until several decades

later that acrylic PSAs as we know them today became commercially available. Modern acrylic PSAs have become important for a number of reasons. Unlike their compounded natural rubber predecessors, they are inherently tacky, colorless polymers that are resistant to oxidation and the attendant problems of discoloration and loss of tack upon aging. In this respect, they are second only to silicone PSAs, over which they have a decided advantage in the cost of materials. The ability to copolymerize with a wide variety of additional non-acrylic monomers leads to a highly versatile technology capable of being delivered in organic solution, aqueous dispersions, or 100% solid forms. In addition, they are amenable to cross-linking via a range of chemical reactions to produce an excellent balance of properties tailored to the particular requirements of numerous applications.

5.2 Composition

Acrylic PSAs are prepared by polymerization, using one of a number of methods to be discussed later, of alkyl esters of acrylic acid with the general structure illustrated in Figure 5.1, where R = H or, in the case of methacrylic esters, R = CH_3, and R′ is an alkyl group.

A homopolymer, even one that is inherently tacky, will not normally possess the desired balance of pressure-sensitive properties to be practically useful. Thus, it is invariably necessary to design a copolymer. Such a copolymer may be prepared from a mixture of acrylic esters and frequently makes use, in addition, of one or more vinyl unsaturated monomers that modify the properties or impart a specific functionality. The patent literature contains literally hundreds of examples of such comonomers. Only those of large commercial significance or that illustrate a particular application will be discussed here. A useful listing with source references, primarily from the patent literature, may be found in Auchter et al. (Ref. 2, pp. 501–508) (see also Chapter 1).

5.2.1 Glass Transition

Before proceeding to the detailed composition, it is necessary to discuss the glass transition and its relationship to monomer selection.

Foremost among the physical property requirements is that the polymer glass transition temperature, T_g, should be well below the intended temperature of bond formation. As depicted in Figure 5.2, at low temperatures the polymer chains have little mobility; thus, the adhesive is stiff and glass-like and characterized by a high modulus of elasticity, G'. As the temperature is increased, the polymer chains acquire, over a range of several degrees (as distinct from a true, sharp thermodynamic transition),

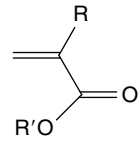


FIGURE 5.1 Chemical structure of an acrylic or methacrylic ester.

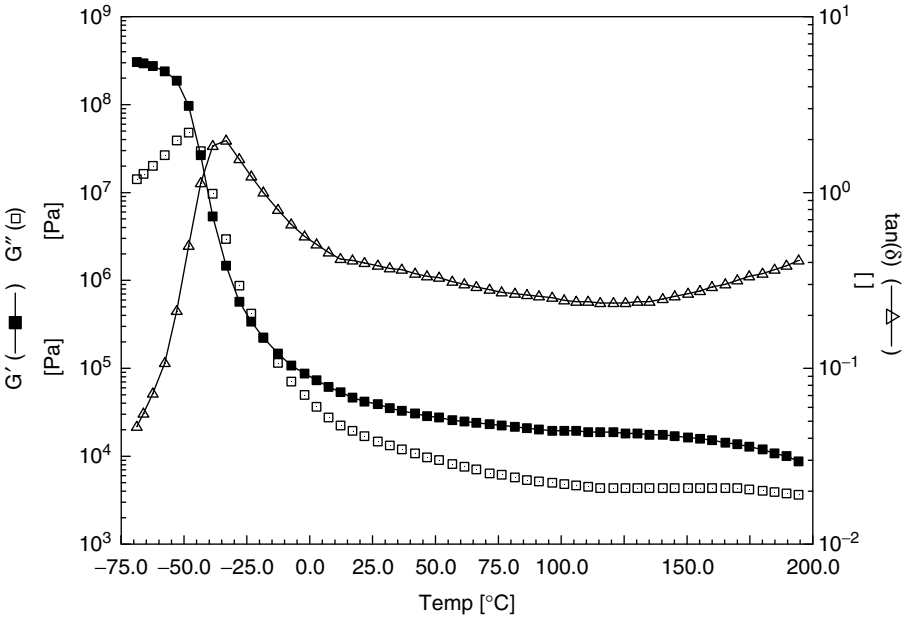


FIGURE 5.2 Temperature dependence of G′, G″, and tan δ for an acrylic PSA.

sufficient thermal energy to permit segmental mobility. This has a dramatic effect on the physical properties as seen from the reduction in modulus. Many other properties that depend upon segmental relaxation rates are similarly affected, including, most importantly for a PSA, tack and creep resistance (see also *Fundamentals of Pressure Sensitivity*, Chapters 6 and 11). The T_g is dependent on the time scale and method of determination (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Thus, some variation is found in the literature for values reported for homopolymers of some of the most important monomers used in the manufacture of acrylic PSAs. Older literature often cites T_g values determined by measurement of brittle point, as illustrated in Figure 5.3. Today, measurement by differential scanning calorimetry (DSC) is preferred but dynamic mechanical analysis (DMA) data are also frequently quoted. In the latter case, the transition temperature is often defined as the maximum in the loss modulus, G'', or, alternatively, the maximum in the tangent of the phase angle, which is given by $\tan \delta = G''/G'$. A self-consistent set of values for some useful monomers, determined by DSC, is given in Table 5.1. From Figure 5.3 one can see that T_g decreases with increasing *n*-alkyl chain up to C_8 for the acrylates and C_{12} for the methacrylates [3]. This is due to increasing free volume created by the alkyl group. The T_g value is known to vary inversely with the free volume and in direct proportion to cohesion energy. The α-methyl groups in the polymethacrylates stiffen the chains and increase the volume required for segmental rotation, hence yielding their correspondingly higher values of T_g. Crystallization of the side chains comes into play as the length of the alkyl group continues, again restricting

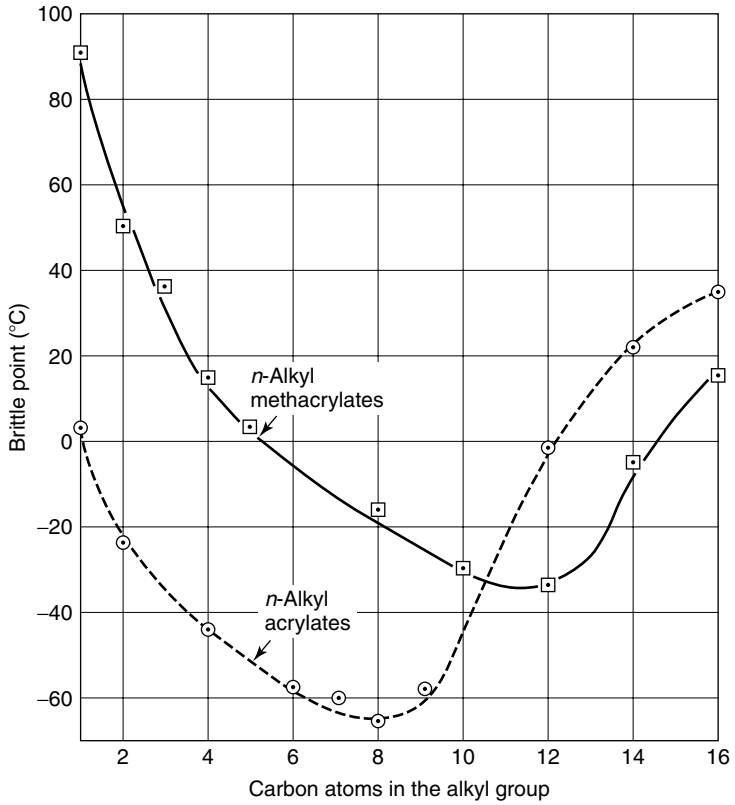


FIGURE 5.3 Brittle points of polymeric n-alkyl acrylates and methacrylates. (Reprinted from *Monomeric Acrylic Esters*, E.H. Riddle, Reinhold Publishing Corp., New York, 1954. With permission.)

mobility and raising the T_g. Note also that, due to the restrictions on segmental movement imposed by their more bulky structures, the branched C_3–C_6 isomers result in higher T_g, as demonstrated by the series *n*-, *iso*-, *sec*-, and *tert*-butyl acrylate (Table 5.1).

A number of nonlinear mixing rules have been proposed to estimate the T_g for a copolymer. Among these, the Fox equation is widely used for its simplicity (see also Chapter 3),

$$\frac{1}{T_{g\,\mathrm{PSA}}} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} + \cdots \tag{5.1}$$

where W_1 and T_{g_1} are, respectively, the weight fraction and homopolymer T_g of monomer 1, etc. (In this equation the unit of temperature is degrees Kelvin.)

For more details on the glass transition temperatures of acrylic monomers and copolymers, see the first section of Chapter 7.

TABLE 5.1 Glass Transition Temperatures of Homopolymers (°C)

Acrylic and Methacrylic Esters			
Alkyl C_n	Alkyl Group	Poly (Acrylate)	Poly (Methacrylate)
C_1	Methyl	22	105
C_2	Ethyl	−8	67
C_3	*n*-Propyl	−25	
C_4	*n*-Butyl	−43	32
	iso-Butyl	−17	64
	sec-Butyl	−6	
	tert-Butyl	55	102
C_6	*n*-Hexyl	−51	−14
C_8	2-Ethylhexyl	−58	
C_{12}	Lauryl	−17	
Polar and functional acrylic and methacrylic polymers			
Acrylic acid	130	Methacrylic acid	162
Acrylamide	220	Methacrylamide	243
Acrylonitrile	105	Methacrylonitrile	112
Other polymers			
Vinyl acetate	42		
Vinyl propionate	8		
Styrene	107		

Method: DSC operated at 20°C/min, midpoint values, for solution- and emulsion-polymerized homopolymers.

Source: Data from Ullman's Encyclopedia of Industrial Chemistry, 5th ed., Vol. A21, p. 169 (1992), VCH. With permission.

5.2.2 Primary Monomers

The primary monomeric component has low homopolymer T_g to ensure a soft, tacky film and typically constitutes from about 50 to about 98 wt % of the polymer. The patent literature often specifies an acrylic ester of a nontertiary C_4–C_{12} alcohol as the primary component. Occasionally, a range of C_4–C_{20} is cited, but in practice the benefit of increasing softness diminishes beyond C_8 linear chain length, as discussed above.

Chains shorter than C_4 do not impart sufficiently low T_g to be considered the primary component. Thus, in practice, the choice is normally reduced to one of a small group of C_4–C_8 monomers that are produced at a commercial scale and yield the desired low-T_g polymer. These are 2-ethylhexyl acrylate (EHA), *iso*-octyl acrylate, and *n*-butyl acrylate (BA). Of these, only 2-ethylhexyl and *n*-butyl are readily available in the merchant monomer market.

Druschke [4] reported the tack and storage modulus as a function of temperature for a series of acrylic ester homopolymers; see Figures 5.4 and 5.5 [4]. As the size of the alkyl group decreases, tack is reduced and the maximum value shifts to a higher temperature. The lower alkyl polyacrylates, polyethyl acrylate and especially polymethyl acrylate, have low tack at normal room temperature. This is consistent with their values

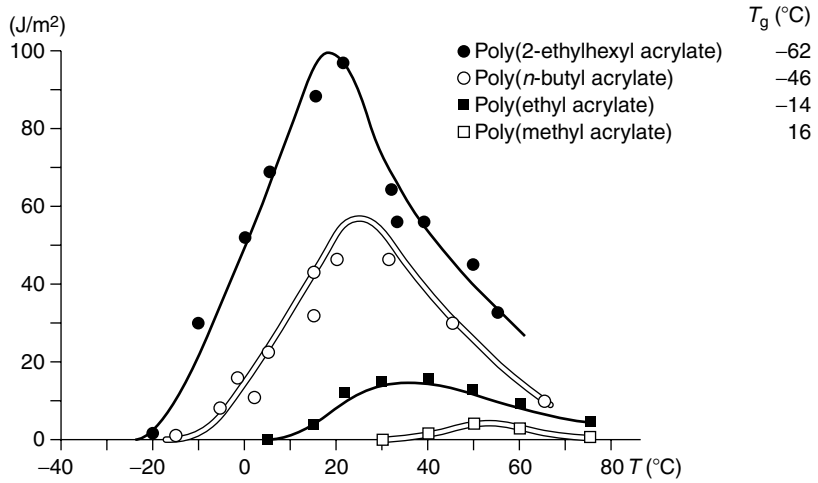


FIGURE 5.4 Tack of various acrylic homopolymers as a function of the temperature. (Reprinted from BASF AG. With permission.)

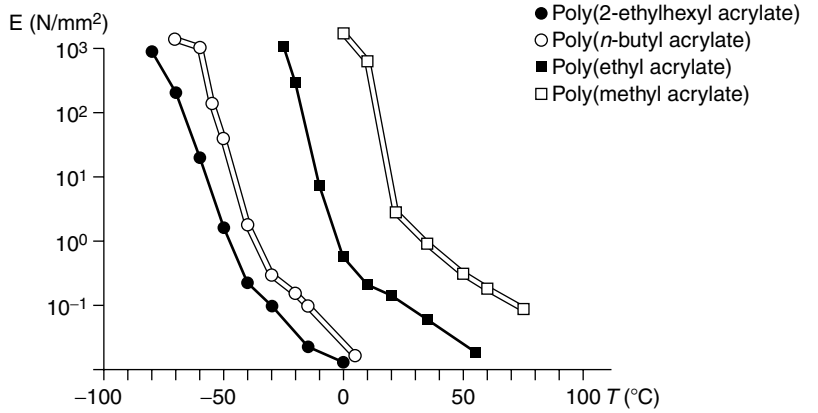


FIGURE 5.5 Modulus of elasticity of various acrylic homopolymers as a function of temperature. (Reprinted from BASF AG. With permission.)

of modulus at 20°C (Figure 5.5), which, in the case of polymethyl acrylate, exceeds the well-known Dahlquist criterion for pressure-sensitive tack, namely that the compression modulus should not be greater than 10^7 dyn/cm^2 (=1 N/mm^2) and preferably less than 10^6 dyn/cm^2 [5]. Only polybutyl acrylate and poly(2-ethylhexyl) acrylate fall within this preferred range of modulus.

5.2.3 Secondary (Modifying) Monomers

Useful PSAs are not homopolymers or even copolymers of just the primary monomer type. Such an adhesive, although undoubtedly tacky, would lack a good balance between tackiness and the cohesive strength needed to resist an applied shear stress

(see also *Fundamentals of Pressure Sensitivity*, Chapter 8), to ensure clean removal (see also Chapter 8) and to resist cold flow, resulting in edge oozing (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Therefore, a comonomer is used to increase modulus and T_g, thereby improving cohesion according to the demands of the application. These hardening comonomers have T_g greater than 0°C. Common choices are methyl acrylate, which is widely but not exclusively used in solution polymers, methyl methacrylate (MMA), vinyl acetate, and styrene (St). These are typically used in the range of about 10–35 wt %, but occasionally up to as high as 50%. Ethyl acrylate finds limited use, mainly in some solvent-borne PSAs. Its homopolymer T_g is intermediate between the soft primary and hardening monomer components. It suffers from an objectionably strong odor, even at low residual levels.

More polar monomers, including those with functional groups, are also used. When used as the sole comonomer in addition to the primary monomers, they perform a dual role of imparting polarity and, in some cases, functionality in addition to raising T_g.

5.2.3.1 Vinyl Acetate

Vinyl acetate (VAc) is sufficiently different from the acrylic and methacrylic secondary comonomers that polymers containing it are often classified as "vinyl acrylics," as distinct from "all acrylics." Where no such distinction is drawn, the term acrylic PSA is usually taken to include those polymers that contain non-acrylic components such as VAc, in addition to the major acrylic monomer. Among the advantages of VAc may be its relatively low cost, contribution to high tack, and improvement of plasticizer resistance (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Plasticized polyvinyl chloride (PVC) is an important carrier material for numerous pressure-sensitive articles and for these applications the vinyl acrylic PSAs are often preferred. It is a much less reactive comonomer in acrylic polymerization. This could be considered a negative feature, but one that can be turned to an advantage to drive down the residual amount of less volatile acrylate monomers; see the discussion in Section 5.4.5.

Disadvantages include a susceptibility to hydrolysis, which may exclude vinyl acrylics from applications requiring the highest degree of chemical resistance and weatherability. They also suffer from a tendency to yellow with age. These aging problems are exacerbated in emulsion PSAs when the pH has been raised with ammonia. A further limitation that is especially important in solution polymerization is an increased rate of chain transfer (discussed in Section 5.4.2) in comparison with the other typical hardening monomers. The result is lower molecular weight, which makes it difficult to meet the shear requirements, especially hot shear, of many industrial tapes (see also *Applications of Pressure-Sensitive Products*, Chapter 8). As a consequence, VAc is most often found in label and vinyl graphic PSAs.

5.2.4 Polar and Functional Monomers

When polar substrates are to be bonded it is desirable to incorporate some polar monomers into the adhesive. These contribute to stronger van der Waals attractions at the interface, thus increasing the thermodynamic work of adhesion, as well as to an increase in cohesion in the bulk adhesive mass via dipole–dipole interactions. At an air interface or when

in contact with a silicone-coated release liner, the polar groups are oriented into the bulk adhesive and away from the surface. Following contact with a more polar surface, they reorient toward that surface, leading to a slow build-up of adhesion with time. In this respect, acrylic PSAs differ from rubber–resin formulations, which typically exhibit high initial peel resistance and relatively little change over time (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Hydrogen bonding, where possible, is also an important contributor to bulk and interfacial interactions, particularly with carboxylic acids.

It is useful to distinguish, among the polar monomers, those that have functional groups. Terminology is not always consistent in defining the functional monomers but here we mean those monomers that, following polymerization, incorporate readily reactive groups into the polymer. These can serve a number of purposes: as potential sites for cross-linking, for creating a grafted polymer in a second synthetic step, or for some other specialized attribute, such as photoinitiation. In many cases the functional monomers are strong hydrogen bond donors. Moderately polar monomers may be used up to about 30 wt %, whereas highly polar functional monomers are normally used up to about 10%. It should be understood that in the foregoing discussions of the various categories of monomer the ranges of use describe only what is typical.

5.2.4.1 Carboxylic Acids

Ulrich's patent [6] was the first to recognize the advantages of including a carboxylic acid, either acrylic, methacrylic, or itaconic acid, as a comonomer. Acrylamide and methacrylamide were also mentioned as useful, strongly polar monomers. Ulrich reported that these monomers imparted *"the required four-fold balance of adhesion, cohesion, stretchiness and elasticity,"* a phrase that has often been recited in the patent literature. Since then, acrylic acid (AA) has become the most widely used and most studied functional monomer. In solution polymers it is the acid functional monomer of choice, whereas in emulsion polymers methacrylic acid (MAA), being less water-soluble than acrylic acid, is also widely used and studied.

Aubrey and Ginosatis [7] studied the peel resistance rate-dependent master curves of BA/AA copolymers (10 wt % AA) covered with a thin coating of BA homopolymer and vice versa. Their objective was to separate the effects of interfacial hydrogen bonding due to the carboxyl group from its effect on energy dissipation in the bulk adhesive. They concluded that the change in viscoelastic properties of the adhesive bulk resulting from inclusion of 10% acrylic acid makes the more important contribution to the increased resistance to peeling. The increase in thermodynamic work of adhesion, estimated to be a factor of 1.5, contributed, but to a lesser extent.

In another noteworthy investigation, PSA-like networks were prepared by Li et al. [8] from either EHA or EHA/AA (10 wt % AA). In both cases the polymers were cross-linked with 10% hexane diol diacrylate and polymerized in the form of elastomeric cylinders, which mimicked the surface characteristics of a PSA. When two of these cylinders are placed in contact, perpendicular to each other, the area of interaction is a circle to which Johnson–Kendall–Roberts contact mechanics can be applied. The results for adhesion energy plotted versus crack speed correlated well with the rate dependence of practical 90° peel tests of a true EHA/AA PSA. They found that acrylic acid enhances the peel resistance of PSA tapes by increasing the threshold adhesion energy and also

by increasing viscous dissipation through a reduction in critical crack speed. As noted by the authors, this is one of the few mathematical correlations that have been made between fundamental measurements of adhesion and a practical test of bond strength.

5.2.4.2 Hydroxyl Functionality

Hydroxyl functional groups, being much less polar than the carboxylic acids, have correspondingly less impact on the properties. Their chief value comes from their ability to react with certain cross-linkers (see Section 4.3.2). They may also be employed when there is a specific objection to using a carboxylic acid, for example, in acid-free archival tapes, in some electronics applications where corrosion is a concern, in transdermal drug delivery where it may be desired to avoid unwanted acid–base interactions with the active ingredient (see also *Applications of Pressure-Sensitive Products*, Chapters 2 and 4), or in situations where a cross-linking entity can diffuse into the adhesive layer from the tape or label backing or from the adherend. An example of the latter might be a PVC stabilizer. Hydroxyethyl acrylate is the most widely used monomer with hydroxyl functionality. For reproducible polymerization, and especially if used at a high level, care must be taken to monitor the level of dimer (diethylene glycol diacrylate), which slowly forms on storage and creates cross-linked chains when polymerized.

Hydroxylic monomers are normally used at low levels, up to about 5%, but very high levels (~30%) have been employed by Brunsveld and Minnigh [9] to impart a substantial increase in the water vapor transmission rate for wound care applications. Similarly high levels of hydroxyl functionality have been reported by Cantor and Wirtanen [10] as an aid to drug solubility in acrylic polymers for transdermal delivery.

5.2.4.3 Acrylamide and Methacrylamide

These primary amides are strongly polar, highly water-soluble monomers that are more easily incorporated into solution polymers than emulsions. As previously mentioned, Ulrich provided the first teaching of the use of methacrylamide and particularly acrylamide, copolymerized at 4 wt % with *iso*-octyl acrylate in a solution polymer, to produce a packaging tape with superior properties [6]. Despite the difficulties arising from their water solubility they are, on occasion, used successfully in emulsion PSAs. For example, Wiest et al. [11] prepared emulsion polymers using ethylene, VAc, and acrylic comonomers in which acrylamide or methacrylamide played a key role in imparting cohesive strength to the resulting PSA.

5.2.4.4 Substituted Amides

Vinyl lactams and aliphatic substituted amides are frequently used polar monomers.

5.2.4.4.1 Vinyl Lactams

N-vinyl pyrrolidone (NVP) is one of the more important, moderately polar specialty monomers. When copolymerized with a main alkyl acrylate ester, but without additional acidic monomers, it has been proposed for use in noncorroding tapes for electrical insulation [12] and for use on automotive paints [13].

As a hydrogen bond acceptor NVP can participate in acid–base interactions with a hydrogen bond donating a comonomer such as acrylic acid for enhanced cohesion [14].

This same invention takes advantage of the hydrophilic nature of NVP to enhance the water vapor transmission rate of the adhesive for use on skin. Similarly, acid–base interactions explain the improved adhesion to PVC surfaces, as discussed by Smith and Smit [15]. In addition to improved anchorage of the adhesive to the substrate, the shrinkage that occurs upon storage is reduced. There are numerous examples in the patent literature describing the use of *N*-vinyl lactam-containing PSAs in contact with PVC, either as a tape or label backing or as the adherend.

In transdermal drug delivery NVP has been used to increase the solubility of estradiol in an acrylic matrix [16]. High levels of NVP raise the T_g, which may be undesirable. To overcome this difficulty, pyrrolidonylethyl acrylate has been used as a comonomer to lower T_g with similar functionality [10,17].

Kenney and coworkers [18] described acrylic emulsion copolymers containing *N*-vinyl caprolactam (NVCL) for use on dry or moist skin, making the adhesive suitable for a variety of medical uses such as bandages, wound dressings, and surgical drapes. Use of NVCL is said to provide the hydrophilicity needed to withstand perspiration and the cohesion required for clean removal. When compared with NVP at 5 wt % in a BA copolymer, NVCL demonstrated superiority in skin adhesion and wear characteristics [18–20]. NVCL containing thermoplastic acrylic hot-melt adhesives for similar applications have been described by Sun and Kenney [21]. They demonstrated good skin adhesion characteristics but rather high melt viscosities, in the range of 40,000 to 350,000 mPa · s at 177°C.

The use of NVP in pressure-sensitive hydrogels has made possible the synthesis of a new class of pressure-sensitive materials based on simultaneous plasticizing cross-linking and has given rise to a new theory of pressure-sensitive adhesion (see also *Fundamentals of Pressure Sensitivity*, Chapter 7, and Chapter 8 in this book).

5.2.4.4.2 Aliphatic Substituted Amides

These have also been found to be very useful components of skin-contacting adhesives. Waldman [22] described an adhesive containing, in addition to a minor amount of cross-linkable alkoxysilyl functionality, 15 wt % N-*tert*-butylacrylamide. This enabled clean removability in a self-wound tape while maintaining sufficient tack. N-substituted acrylamide, particularly *t*-octylacrylamide, has been mentioned by Silverberg et al. as a preferred monomer for building cohesion in an adhesive that is free from active hydrogen containing monomers or cross-linker for use in transdermal drug delivery patches [23]. It has also been found to impart resistance to plasticization by skin penetration enhancers, a common excipient in patches [24].

5.2.4.5 Molecular Weight and Viscoelasticity

Molecular weight is of great importance to pressure-sensitive properties. Low molecular weight may improve tack but this is by no means sufficient for a useful PSA, which must have sufficient cohesion to peel cleanly from a surface and bear the required load.

It is helpful to recall the viscoelastic properties as a function of temperature (Figure 5.2). At low temperatures, where the adhesive is glassy, relaxation times are very long and the local mobility of the polymer chains is affected by the selection of monomers, which determine the glass transition temperature. In the region above the transition, the modulus drops rapidly as short chain segments relax. The degree to which

the storage modulus falls, that is, the plateau modulus, is inversely proportional to the molecular weight between chain entanglements, denoted by M_e. As the temperature continues to increase, the modulus remains approximately constant through the plateau region until the terminal zone, where the chains become disentangled and viscous flow occurs. Higher molecular weight shifts the onset of flow to higher temperature. At higher molecular weight, polymer relaxation times are increased and there is a substantial improvement in creep resistance, as expected because zero shear viscosity increases with molecular weight as $M^{3.4}$ above the entanglement molecular weight. Peel and tack are less sensitive to change in molecular weight than shear holding power. Druschke [4] compared a series of acrylic polymers differing only in molecular weight and demonstrated that at *K* values above 50, in a regime of adhesion failure, both peel and tack decrease slightly with increasing molecular weight.

Low plateau modulus (high M_e) is desirable for rapid bond development and at the same time contributes to fibrillation during debonding. Entanglement molecular weight can be positively influenced by choosing branched monomers, for example, EHA rather than BA. Branched vinyl esters have also been suggested for this purpose. Yang [25] has measured M_e for several homopolymers by DMA using the relationship $M_e = \rho RT/G_n^0$ where ρ is the density, *R* is the gas constant, *T* is the temperature, and G_n^0 is the plateau modulus. For poly(vinyl neodecanoate) he obtained $M_e \simeq 70{,}000$ compared with 35,000 for poly(2-ethylhexyl acrylate) and 17,000 for poly(butyl acrylate) [25]. The T_g of poly(vinyl decanoate), determined from the maximum of the loss modulus, was measured as 0°C. This makes it useful as a slightly hardening comonomer.

Yang [26] demonstrated that the ratio of loss modulus, *G″*, to storage modulus, *G′*, measured at the bonding and debonding frequencies, respectively, correlates well with measured peel resistance for a series of acrylic copolymers (Figures 5.6 and 5.7) [26].

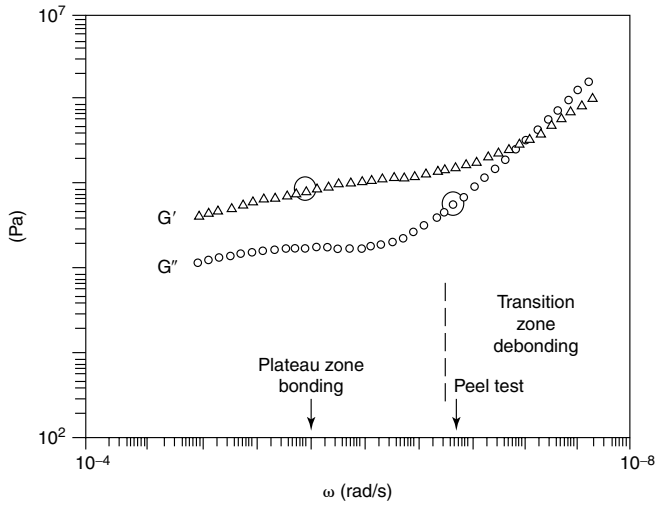


FIGURE 5.6 G′ and G″ of poly(n-butyl acrylate). (Reprinted from Yang, H.W.H., *J. Appl. Polym. Sci*., 55(4), 647, 1995. With permission.)

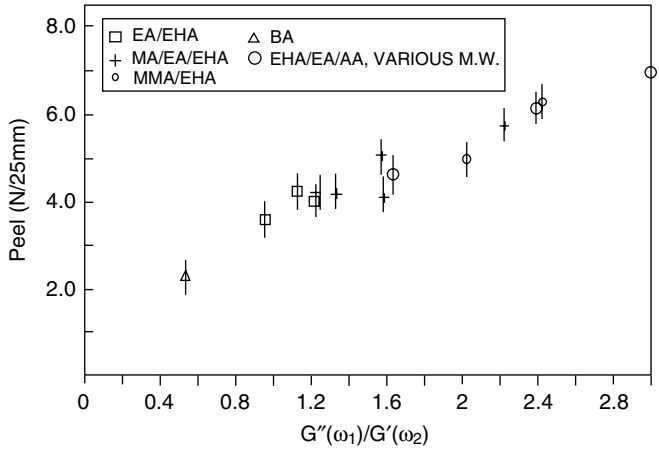


FIGURE 5.7 Dependence of peel strength on G″/G′. (Reprinted from Yang, H.W.H., *J. Appl. Polym. Sci.*, 55(4), 647, 1995. With permission.)

(This issue has been also discussed in *Fundamentals of Pressure Sensitivity,* Chapter 6, and also in *Applications of Pressure-Sensitive Products*, Chapter 8).

5.3 Cross-Linking and Physical Interactions

Cross-linking is an indispensable tool for achieving high cohesive strength and a large body of literature and patents have been devoted to this subject (see also Chapter 8). In particular, it is difficult to achieve sufficient cohesive strength in a solvent-borne acrylic without cross-linking due to the restrictions on molecular weight imposed by the requirement for a coatable solution viscosity (see also Chapter 10). Czech has published extensively on the subject of cross-linking solvent-borne acrylic PSAs and much of his work has been collected in a monograph to which the interested reader is referred for a comprehensive discussion [27]. Emulsion PSAs, due to the independence of viscosity on molecular weight, are less dependent upon cross-linking to achieve cohesion. Nonetheless, cross-linking is often practiced here as well. The effectiveness of cross-linking a water-borne coating depends very much upon the distribution of functional monomers within the heterogeneous coating and upon the particle–particle interphase, as illustrated by the work of Zosel [28]. Thermoplastic acrylic hot-melt PSAs (HMPSAs) require some method of cross-linking, whether it be a thermally reversible physical or chemical interaction or a postcoating irradiation, to have useful properties.

5.3.1 Physical Interactions

Physical associations, whether resulting from van der Waals forces, which may be considered collectively to include interactions resulting from electrostatic charge, dipoles, and hydrogen bonding, or from a microphase separation, are effective as a means to

increase cohesive strength. Unlike covalent bonds, however, they are readily reversed with a moderate increase in temperature. Effects of noncovalent reversible cross-linking, due to hydrogen, electrostatic, or ionic bonding between complementary functional groups, on adhesion and mechanical properties of polymer blends are described in further detail in Chapter 7.

5.3.1.1 Interactions between Polar Monomers

As discussed above, highly polar functional monomers such as AA or acrylamide interact strongly via hydrogen bonding and dipole–dipole interactions to impart shear strength to a PSA. At the bond interface they similarly contribute to adhesive forces. Combinations of polar monomers have also been used to enhance PSA properties. For example, Warson and colleagues [29,30] used hydroxypropyl acrylate in combination with either MAA or AA to create an emulsion PSA suitable for sealing cardboard cartons in which there is considerable bursting strain.

Skoglund [31] combined acrylamide and AA in a single emulsion copolymer or separately in a blend of polymers to create a removable PSA. The strong hydrogen bonding interactions were believed to be responsible for the removable properties.

5.3.1.2 Ionic Interactions

Acid–base interactions have been shown to be capable of achieving a thermally reversible, ionically cross-linked network. Guerin et al. [32] used a blend of a low T_g carboxylic acid functional PSA with a higher T_g compatible amine functional polyacrylate to create a pressure-sensitive acrylic HMPSA. Typical amines used were *t*-butyl- or dimethylaminoethyl methacrylate (*t*-BAEMA, DMAEMA). Similar systems have been studied in greater detail by Everaerts et al. [33]. They found that a tertiary amine such as DMAEMA interacts strongly, but reversibly, with AA and demonstrated that the onset of flow upon heating is controlled by the strength of the acid–base interactions, rather than the T_g of the polymer, in contrast to phase-separated block copolymer formulations. This makes HMPSAs with higher service temperature possible. A copolymer containing both AA and DMAEMA demonstrated much lower cohesive strength, which was attributed to a preponderance of *intra*molecular rather than *inter*molecular interactions. They also demonstrated that when primary or secondary amine functionality is present in the cross-linker, a thermosetting adhesive is obtained by heating to elevated temperature. In earlier work, Samour [34] prepared solutions of acrylic PSAs containing approximately equimolar concentrations of acidic and basic comonomers such as *t*-BAEMA or DMAEMA for a nonirritating skin-contacting PSA. In this case, the adhesive was coated from solution and hence thermal reversibility was not a consideration.

Zwitterionic monomers such as betaines and aminimides have been used by Knoepfel and Silver [35] to build cohesion by intermolecular ionic association. When used in amounts up to 20 wt %, preferably 1–10%, the adhesives exhibited outstanding shear strength combined with excellent tack and peel resistance. Zwitterionic monomers were also suggested as an optional component of an emulsion PSA possessing a broad range of service temperatures [36].

5.3.1.3 Effect of Neutralization

Neutralization of a carboxyl functional polymer with a *mono*valent metal cation has a profound effect on cohesive strength. This is presumably due to interactions of the strong dipoles that result. Satas and Mihalik examined in detail the effect of bound sodium on pressure-sensitive properties and found it to be an effective method of increasing cohesive strength, with decreased tack and peel force, as expected [37]. Blake [38] prepared a water-dispersible PSA by partially neutralizing a tackified acrylic emulsion with potassium hydroxide in combination with sodium or lithium hydroxide. He determined that KOH, when used alone, gave good tack but low shear strength, whereas NaOH and LiOH had the reverse effect. Similarly, Midgley [39] observed that the smaller the ion size of the alkali, the greater the improvement in shear. As demonstrated by Feldstein et al. in Chapter 7, ionization of carboxylic and amino groups in the blends of acrylic copolymers leads to tack improvement.

5.3.1.4 Physical Cross-Links Due to Phase Separation

The typical acrylic PSA produced by free radical polymerization has a statistical distribution of monomers determined by the monomer reactivity ratios and further influenced by the timing of addition. In most cases, the polymers may be regarded as completely random with the same distribution in every chain [2]. These polymers are characterized by a single glass transition. However, when there is a large disparity in monomer reactivity it is possible, even in a simple free radical addition polymerization, to achieve a phase separation into domains rich in one or another of the monomers. This has been demonstrated by Chu et al. [40], who copolymerized VAc (monomer 1) and BA (monomer 2) in a bulk photopolymerization and then annealed the resulting polymer at 70°C. For this pair of monomers the respective reactivity ratios are $r_1 = 0.0018$ and $r_2 = 3.48$. (Each r is the ratio of the rate constant for a reactive propagating chain end to add the same monomer to the rate constant for addition of the comonomer.) They obtained good damping over a wide temperature range with two distinct glass transitions.

Recently, acrylic block copolymers of MMA–BA–MMA prepared by anionic polymerization have become available. These offer the possibility of compounding with tackifying resins in a manner analogous to styrene–isoprene–styrene (SIS) or styrene–butadiene–styrene rubbers, cohesive strength coming from physical association of the end-blocks. This topic is discussed by Hu and Paul in Chapter 3; (see also Chapters 1 and 8).

Macromolecular monomers (macromers) provide another convenient means of achieving a degree of microphase separation (see also Chapter 1). To impart cohesion, the macromer should have a high glass transition temperature. When polymerized with conventional monomers, a graft (sometimes called a comb) polymer architecture is formed. Macromers are synthesized by anionic polymerization and have a molecular weight typically in the range 5,000–50,000 and, more preferably, 12,000–25,000, with narrow polydispersity [41]. They are terminated at one end with a vinyl copolymerizable group such as a methacrylate. In PSAs the commercially available polystyrene and poly(methyl methacrylate) (PMMA) macromers are most commonly used. Microphase separation of the pendant macromer chains creates thermally reversible

physical cross-links. The phase morphology of block copolymers with well-defined architecture has been widely studied; see, for example, Hamley [42]. As used in acrylic PSAs, however, there is a random distribution of grafts attached to a main polyacrylate copolymer backbone of wide molecular weight distribution. Hence, a strongly ordered segregation should not be expected, but despite this the approach has proved to be effective.

Schlademan [43] described acrylic PSAs prepared with vinyl aromatic macromers. The adhesive properties of such PSAs, prepared with 2-polystyrylethyl methacrylate, molecular weight 13,000, were discussed by Mancinelli and Norris [44]. They demonstrated that a polymer containing 10% macromer could be compounded with a large amount of rosin ester tackifier and plasticizer to meet the requirements of tape applications, but at the expense of hot shear resistance. Mancinelli also reported on acrylic HMPSAs containing a PMMA macromer that can be plasticized and tackified with hydrogenated rosin esters or hydrogenated styrene and α-methyl styrene resins [45–47]. Husman et al. [48] similarly described acrylic PSAs prepared with macromers with $T_g > 20°C$ and provided examples of the use of macromers of PMMA, as well as vinyl aromatic monomers. Polystyrene macromer has been used to reinforce a skin-contacting adhesive to prevent objectionable build-up in adhesion over time [49].

Nakamae et al. [50] compared the PSA properties of random BA/styrene copolymers prepared in solution with polymers in which either monomer was introduced separately as a macromer. Polystyrene introduced as a macromer gave much higher shear strength, but these polymers were also higher in molecular weight, thus complicating interpretation of the data. A graft structure was inferred from evidence of surface activity in measurements of interfacial tension at a water–toluene interface. In a second paper [51], they prepared polymers of BA-co-MMA-*g*-St and BA-*co*-MMA-*co*-St in which the total hard monomer component was 20 wt % and the ratio of the two components, MMA and poly(styrene) macromer or MMA and styrene monomer, was varied. Here, care was taken to perform comparisons at similar molecular weights. The authors demonstrated that the macromer, when used alone at 20%, had a large impact on the cohesive strength compared with styrene monomer. Furthermore, there was less reduction in tack when the macromer was used. Transmission electron microscopy was used to verify that microphase separation occurred, beginning to be observable at 10% and clearly defined at 15 and 20% macromer.

5.3.2 Chemical Cross-Linking

It is convenient to distinguish between chemical cross-linking, which involves only functional groups attached to the polymer, sometimes referred to as internal cross-linking, and reactions that require an additional reagent. In both cases some reactions will proceed rapidly under ambient curing conditions, whereas others require heating and perhaps a catalyst (see also Chapter 8). Many of the chemistries employed in cross-linking acrylic PSAs have been borrowed and adapted from the metal and textile coatings industries or from the vulcanization of rubber. The chief differences are that PSAs are only lightly cross-linked to preserve viscoelastic properties and reactions that require substantial heat input are not practical for PSAs coated on a continuous web.

The challenge in cross-linking any PSA is to ensure that the process is reproducibly completed within some reasonable time (at most, some days) following coating and that further reaction does not occur during storage of the finished article, causing an unwanted change in properties, particularly a loss of tack.

5.3.2.1 Cross-Linking (Gel Formation) during Polymerization

Cross-linking may be achieved during the polymerization process by the deliberate inclusion of a multifunctional monomer or by virtue of the chain transfer processes, which are inherent in emulsion polymerization.

5.3.2.1.1 Chain Transfer to Polymer

Cross-linking can occur during polymerization by chain transfer to polymer. (See Section 5.4.2 below for an explanation of chain transfer.) In an emulsion polymerization under the usual conditions of high instantaneous conversion, that is, low monomer and high polymer concentration within the particle, chain transfer to polymer leading to branching is highly favored. Gel networks form within the particle when the ends of long-chain branches produced by intermolecular chain transfer meet and terminate by combination (see also Chapter 1). Lovell et al. [52] used ^{13}C nuclear magnetic resonance (NMR) to study this process in emulsion copolymers of BA. They demonstrated that chain transfer to polymer occurs by hydrogen abstraction at the backbone tertiary carbon, as expected, and found branching to the extent of 2–4 mol % corresponding to 10–20 branches per thousand backbone carbon atoms; see Figure 5.8. Intraparticle cross-linking is thus a normal result of BA emulsion polymerization and a chain transfer agent which can compete efficiently, such as dodecyl mercaptan (DDM), must be added should it be necessary to moderate this. In model studies of BA homopolymer emulsions, Zosel and Ley [53] reported that the addition of 0.06 wt % DDM resulted

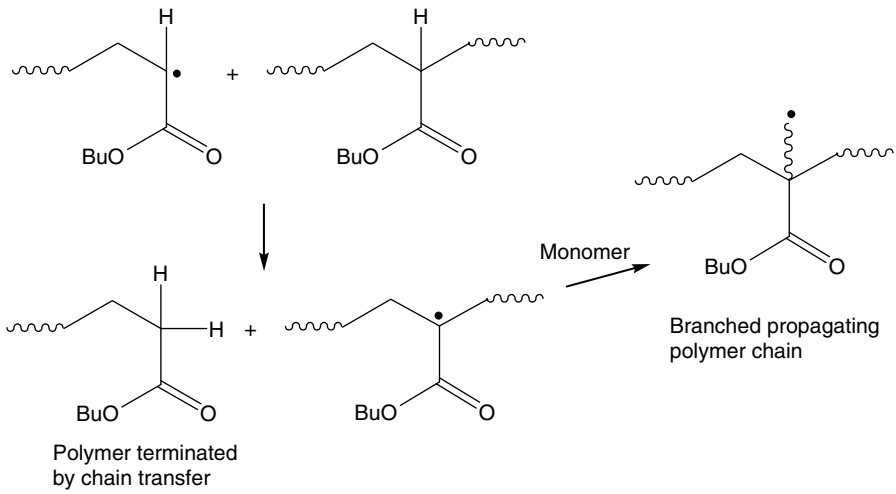


FIGURE 5.8 Chain transfer to polymer in polymerization of n-butyl acrylate.

in a polymer near the gel point, as evidenced by the linear viscoelastic response $G' \simeq G'' \propto \omega^{1/2}$ at low frequency ω. Only at higher levels of DDM was an uncross-linked polymer formed. Plessis et al. [54] developed a mathematical model to describe the effect of DDM on the kinetics and structural properties of an emulsion polymerization of BA. The model correctly predicted that the presence of modest amounts of chain transfer agent (CTA) makes chain transfer the dominant mechanism for termination. As termination by combination becomes less important, the gel content is reduced. The number of branches, determined by quantifying the quaternary carbons using solid-state NMR spectroscopy, was almost independent of the level of CTA. The CTA only affected the length of the long-chain branches and the model predicted that most of the branches were short branches produced by intramolecular chain transfer to polymer, that is, by backbiting reactions.

Heatley et al. [55] demonstrated that the level of chain transfer to polymer is much higher for 2-EHA than for BA homopolymerized under the same conditions. Britton and coworkers [56] studied copolymers of BA with VAc, MMA, and St. Compared with the corresponding homopolymers they reported higher levels of chain transfer to polymer in VAc/BA copolymers due to hydrogen abstraction at BA backbone tertiary C–H bonds by the highly reactive VAc-ended chain radicals. In contrast, St and, to a lesser extent, MMA disproportionately reduced the level of branching.

5.3.2.1.2 Multifunctional Monomers

In emulsion acrylic PSAs, due to gel formation created by chain transfer to polymer, it is usually unnecessary to add a multifunctional monomer to create cross-links within the particle. Nonetheless, there are occasional examples within the patent literature; for example, Ryrfors and Hassander [57] have described the use of triacrylates of trimethylolpropane or pentaerythritol and tetraallylethane in an emulsion PSA as cross-linking monomer.

Other examples, although suggesting use in emulsions, appear to be intended primarily for developing cohesion in solution polymers. One such example is the study by Ono and Matsuguma [58], who used poly(ethylene glycol) (PEG) dimethacrylate to impart cohesion as a way to avoid using high levels of polar monomers in a skin-contacting tape or surgical drape. The useful amounts are necessarily low: at concentrations above 0.05 mol %, gelation occurred.

5.3.2.2 Internal Postpolymerization Cross-Linking

Cross-link formation following the polymerization and subsequent coating process has a number of advantages. Chief among these is the ability to develop cross-links between adjacent emulsion particles following film formation and, in the case of solution polymers, to permit a higher solids content coating solution. Several chemistries have been employed to create cross-links between pendant functional groups on the polymer. The most used include epoxides and, to a lesser extent, *N*-alkoxy amides, and organosilanes.

5.3.2.2.1 Epoxides

Glycidyl methacrylate (GMA) is the most commonly used epoxide monomer and is used in both solution and emulsion polymers, where, according to Warson [29], only

about 7% of the starting epoxide is normally hydrolyzed, leaving most available for cross-linking. Its use at low levels has been well established for many years. Kordzinski and Horn [59] heated a PSA film containing glycidyl functionality to a temperature above 100°C to cross-link by homopolymerization of the epoxide. More typically, a carboxylic acid or anhydride is chosen to coreact with the epoxide. For example, Knapp [60] prepared a PSA containing 5 wt % acrylic acid and 1% GMA and determined that the viscosity of the polymer solution at 45% solids remained stable for at least 3 months of room temperature storage but cross-linked at room temperature when dried. Lehmann and Curts [61,62] used a Lewis acid catalyst such as zinc chloride to accelerate the cure of glycidyl monomers used in combination with carboxylic acids, acid anhydrides, or diketene. They obtained full cure in 2 to 7 min at temperatures between 60 and 100°C. The catalyst, however, is a second component that must be added just prior to coating.

Recently, Van Wijk-Schmitz and coworkers demonstrated that it is possible to improve upon the stability of Knapp's compositions by including, in addition to the epoxide, a bulky polycyclic aliphatic monomer such as isobornyl acrylate [63]. Satisfactory solution stability was demonstrated at 50% solids or more with compositions containing 1 to 7 mol % GMA in a one-component PSA.

5.3.2.2.2 **N-*Alkoxy Amides***

Whereas acrylamide tends to partition into the water phase during emulsion polymerization producing polyacrylamide, the less soluble *N*-alkoxy acrylamides, especially the higher alkanols, are more easily copolymerized into emulsion PSAs for use as internal cross-linking agents. Reaction of *N*-methylolacrylamide (NMA) has been proposed to proceed by a self-condensation releasing formaldehyde and water. *N*-methylolacrylamide is frequently mentioned in the PSA patent literature as one of a list of possible cross-linking monomers, but rarely constitutes a required element of the claimed composition. Thus, it does not appear to have been widely used in commercial practice. This is undoubtedly explained by the thermal curing requirements. However, there are a few examples that are dependent upon cross-linking via NMA. The earliest use was by Coffman [64], who copolymerized a small amount into a carboxylated solvent-borne PSA where it could react with the acid as well as self-condense. The cross-linking reaction required heating for 15 min at 140°C. Use of a strong acid catalyst to accelerate the cure would be undesirable in many end uses. In another example, Grabemann and Hauber [65] used mixtures of acrylic emulsions containing AA and NMA for use in manually tearable adhesive tapes. Mueller and coworkers [66] used NMA as a component monomer in a peelable label water-borne PSA.

An approach to reducing the cure time and temperature without resorting to a strong acid catalyst has been described in which methyl acrylamidoglycolate methyl ether (MAGME) was used in combination with a more reactive monomer, such as an organofunctional silane [67]. Using a cure time of 5 to 7 min at 100°C, the authors were able to achieve much improved cohesion compared with MAGME used alone or catalyzed with *p*-toluene sulfonic acid and hypothesized that condensation of the silane initiated low-temperature condensation of MAGME. Because the result for the silane used alone was not reported, it is difficult to assess the effectiveness of this as a general approach.

Another method of enabling low-temperature cure without the need for a postcure has been described by Seiho [68]. Here, two acrylic copolymers were mixed, one containing NMA and the other containing OH functional monomer and 2-acrylamido-2-methylpropane sulfonic acid.

Aside from the difficulty in achieving full cure under normal drying conditions, the evolution of formaldehyde is a further disincentive to using NMA in today's coatings and PSAs due to its toxicity. In a study to understand the effect on shear holding power of cross-linking a water-borne PSA, Tobing and Klein [69] investigated the reaction of *iso*-butoxymethacrylamide (IBMA) in an emulsion containing AA. IBMA is less reactive than NMA and typically requires heating at ~175°C to effect curing. In this study, where limited reaction was required to graft entangled soluble polymer to the microgel fraction, heating for 10 min at 121°C was sufficient to achieve cross-linking across emulsion particle boundaries, resulting in a high shear strength adhesive. Clearly, this study was not intended to suggest a more practical cure time, but rather to elucidate the mechanisms for cross-linking in emulsion PSAs.

5.3.2.2.3 Organosilanes

Ethylenically unsaturated alkoxysilanes such as γ-methacryloxypropyl trimethoxysilane have occasionally been used as self-cross-linking monomers. The alkoxy groups undergo hydrolysis to silanols and condense to form siloxane cross-links. Senkus et al. [70] used this method to cross-link PSA microparticulate beads prepared by aqueous suspension polymerization. Walker and Foreman [71] prepared siloxane cross-linked water-borne PSAs that exhibited clean removability and little increase in peel resistance with time following bond formation.

5.3.2.3 Stable, Externally Cross-Linked One-Component Systems

Self-curing PSAs are one-component adhesives that eliminate the need for the user to add a cross-linker just prior to use, thus avoiding the problems of possible weighing errors and wasted materials due to the limited mixed pot life of two-component adhesives. The price for this convenience, of course, is less flexibility to adjust the properties at the time of use.

5.3.2.3.1 Organometallic Cross-Linkers

Early self-curing solvent-borne PSAs utilized metal alkoxide cross-linkers [72]. The reactions are illustrated in Figure 5.9. The reaction proceeds to completion upon drying, driven by the evaporation of the alcohol. The ability of additional alkoxide groups to react (beyond the two required to create a cross-link) will depend upon steric considerations. Any unreacted alkoxide ligands are prone to hydrolysis. Titanium alkoxides such as tetraisopropyl titanate, $Ti(OC_3H_7)_4$, and tetra-*n*-butyl titanate, $Ti(OC_4H_9)_4$, are especially preferred but have the disadvantage of imparting a yellow color to the adhesive, thus limiting their usefulness in many applications. Furthermore, they are highly reactive, undergoing alcoholysis at room temperature in the absence of any catalyst, and are therefore restricted to use with hydroxyl functional polymers. Exposure to water must be avoided because they hydrolyze rapidly. Stabilization in solution, enabling a one-component system, is in principle achieved by the addition of a high molar excess of

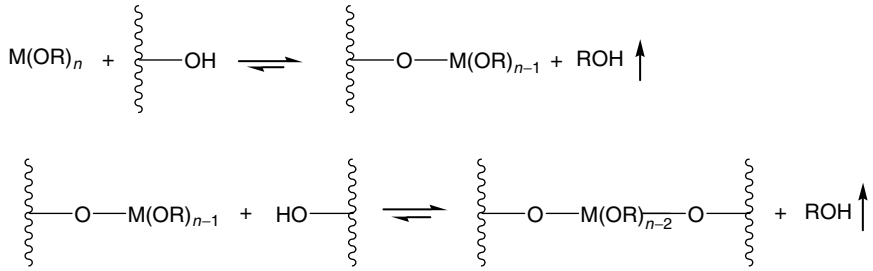


FIGURE 5.9 Cross-linking by metal alkoxides.

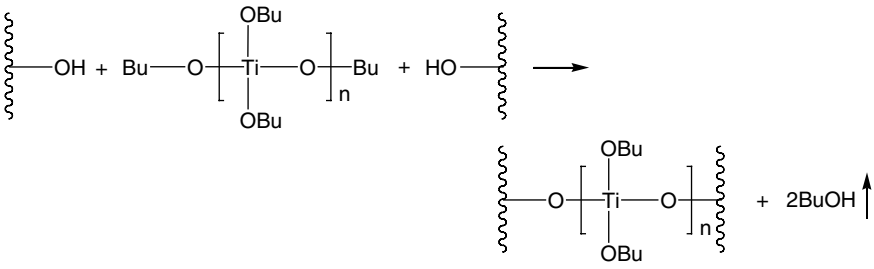


FIGURE 5.10 Cross-linking by poly(butyl titanate).

a lower alcohol. In reality, the solution stability is marginal and a viscosity increase may be noted upon storage, resulting in a "stringy" solution with poor coating properties. Such systems are no longer in commercial use.

An improvement was the introduction by McKenna et al. [73] of polymetaloxane cross-linkers based on titanium or zirconium including, in particular, poly(butyl titanate). This cross-linker provides a lighter color and improved stability in solution compared with the monomeric titanates. Proposed originally as a cross-linker for either hydroxyl or carboxyl groups, it continues in small commercial use today because of its utility in cross-linking hydroxyl functional polymers. In the cross-linking reaction illustrated in Figure 5.10, the terminal titanium atoms are in an octahedral state, which reverts to a less reactive tetrahedral geometry following the reaction of one of the attached butoxide ligands.

An important innovation was the development of chelated metal cross-linkers. McKenna [74] used chelated titanium to cross-link hydroxyl functional polymers. A preferred cross-linker is diisopropoxybis(acetylacetone)titanate, sold under the tradenames Tyzor® AA or Tyzor GBA (E.I. Du Pont de Nemours, Wilmington, Delaware) and has the structure illustrated in Figure 5.11. The isopropoxide groups react with polymer-bound hydroxyl or carboxyl groups to create a cross-linked network in a manner analogous to the reaction of unchelated alkoxides. As before, solution stabilization is achieved with an excess of alcohol, but compared with an unchelated titanium alkoxide the resulting solution is much more stable. The disadvantage of a distinct yellow color also applies here. Furthermore, the curing kinetics with hydroxyl groups is rather slow and additional time and temperature are needed for effective curing.

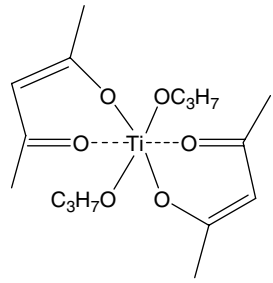
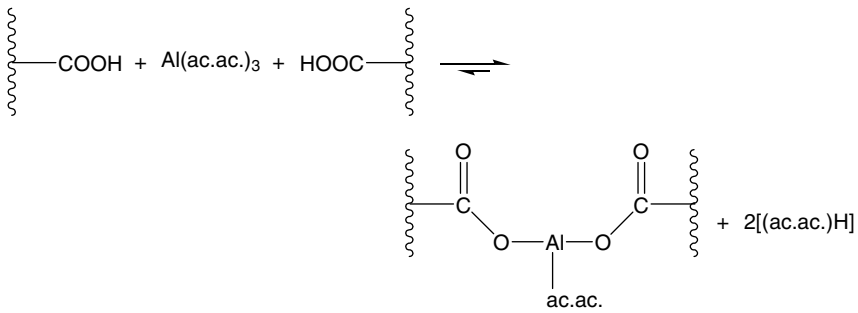


FIGURE 5.11 Chelated titanium alkoxide cross-linker.



where (ac.ac.) = acetylacetonate ligand and (ac.ac.) H = acetyl acetone or 2,4-pentanedione

FIGURE 5.12 First stage of cross-linking with aluminum acetyl acetonate.

Czech [27, p. 31] considered the reaction unsuitable for practical use unless carboxyl groups are also present, but others reported it was useful in situations where carboxyl functionality is undesirable such as, for example, adhesion to nonpolar substrates [75].

The key to the widespread adoption of self-curing solutions was the introduction by Anderson et al. of aluminum tris(acetylacetonate) as a cross-linker [76]. This enabled the development of stable solutions of carboxylated polymers with a colorless film, which were therefore useful in a host of clear film label and graphic arts applications. Today, together with the use of chelated titanium for some tape applications where color is less important, this is the most important chemistry for self-curing acrylic solution polymers and it dominates the merchant market for acrylic solutions in the United States and Europe. In contrast, despite early Japanese recognition of the chemistry for cross-linking hard acrylic coating compositions [77], it has not thus far proved as popular in Asia for pressure-sensitive materials where two-part systems are generally used. The first stage of the cross-linking reaction is illustrated in Figure 5.12.

Acetyl acetone exhibits keto-enol tautomerism and, in its pure form, exists primarily in the enol configuration with $pK_a \simeq 9$. Hence, replacement by the more acidic polymer-bound carboxyl groups proceeds readily, even advancing at room temperature, whereas reaction with weakly acidic hydroxyl groups requires a longer period of heating than is typically achieved in a production drying oven. Because the reaction is driven by the

removal of pentanedione, it is common to add a small amount of pentanedione to the solution, in addition to a lower alcohol, to prevent viscosity increase during storage. It is important not to add too much because the boiling point is 139°C. It is normally recommended that self-curing coatings should be dried to less than about 1% residual solvent and ideally to less than 0.5% to achieve full cure. Under these conditions, cross-linking is substantially completed within a few days of ambient roll storage.

When hydroxyl and carboxyl groups are used in combination and cross-linked with a chelated metal, Czech [27] observed unexpected synergism, shown in higher shear strength especially at 70°C and above. However, it should be noted that hydroxyl groups have the potential for *inter-* or *intra*polymer esterification with carboxylic acid in the presence of an esterification catalyst. Aluminum tris(acetyl acetate) and the titanium compounds are Lewis acids capable of catalyzing this reaction. The result is a gradual increase in high-temperature modulus upon storage, indicative of continued cross-linking.

5.3.2.3.2 Metal Salts

Polyvalent metal salts are commonly used to cross-link carboxyl functional waterborne PSAs. In an early example, Citrone and Oliver [78] determined that many metal salts, oxides, or hydroxides could be used for cross-linking but that normal and basic acetates such as zinc acetate, basic aluminum acetate, and basic zirconyl acetate, as well as basic aluminum formate, were especially useful when used at a concentration of 0.025 to 0.125 mol/mol acid. Not mentioned, but desirable, is that the salt should be soluble at moderately alkaline pH, thus enabling the use of ammonia, for example, for neutralization. A disadvantage of using basic aluminum acetate is that upon raising the pH, the acetate ligand is easily replaced by a hydroxyl to form aluminum hydroxide, which has very low solubility between pH 4 and 9.5 [79]. Sanderson and Zdanowski [80] also employed polyvalent metal salts, finding that fugitive amine and especially ammonia complexes of zinc, cadmium, or zirconium were particularly useful. Chelates with amino acids such as glycine or alanine were exemplified. These are soluble in aqueous ammonia, creating a complex such as zinc ammonium glycinate, which forms ionic cross-links with carboxyl functional polymers upon drying and volatilization of the ammonia.

5.3.2.3.3 Hydrazines

An interesting variation on self-cross-linking PSA solutions (or, alternatively, nonaqueous dispersions) was devised by Buensch and Druschke [81], who cross-linked via polymerizable ketones or aldehydes such as methylvinyl ketone, acetonyl acrylate, and α-ethylacrolein. The cross-linking entity is a polyhydrazine compound stabilized in solution with a fivefold or more molar excess of a volatile monoketone or monoaldehyde. Cross-linking occurs upon drying analogous to the more familiar carboxylated self-curing PSA solutions.

5.3.2.4 Two-Component Systems

There is an extensive body of literature, particularly patents, concerning two-component cross-linking. Representative examples for the different types of chemical reaction will be discussed here.

5.3.2.4.1 Polyfunctional Isocyanates

This is the most widely employed two-component chemistry for solvent-borne PSAs. There are a number of reasons for this: favorable kinetics allowing full cure to develop under normal ambient storage conditions or mildly elevated temperature, useful pot life, and an absence of toxic by-products. However, isocyanate compounds, if volatile, present an inhalation hazard. Thus, many types of polyisocyanate cross-linker are commercially available for safer handling in the form of prepolymers with a low-molecular-weight polyol. Also available are biurets and isocyanurates of aliphatic, cycloaliphatic, and aromatic diisocyanates. In practice, many of these materials are not sufficiently reactive for use with PSAs without heat or catalysis. One of the most commonly employed isocyanate cross-linkers for PSAs is a 3:1 molar adduct of toluene diisocyanate (TDI) with trimethylol propane available, for example, as a 75% solution under the tradename Coronate® L from Nippon Polyurethane Ind., Inc.

Among the first to describe polyisocyanate cross-linking of PSAs were Zang and Lader [82]. They disclosed utility for cross-linking PSAs containing any active hydrogen, including hydroxyl and amide groups, but preferably carboxylic acids. Their preferred ratio of NCO to functional group was from about 0.2 to about 0.5. A copolymer of 2-EHA, VAc, and AA was cross-linked with an NCO-terminated adduct of TDI and castor oil. When coated on various vinyl backings, some highly plasticized, and subjected to accelerated aging conditions, the cross-linked PSA demonstrated excellent retention of peel resistance.

In a recent series of papers, Asahara and coworkers studied the reaction of Coronate L with an acrylic PSA containing 5 wt % 2-hydroxyethyl methacrylate using attenuated total reflectance/Fourier transform infrared (ATR-FTIR) spectroscopy to monitor the cure. In the first study [83] the cross-linker was added at 3 wt % on polymer (NCO/OH ratio 0.1) in dilute solution, applied in a thin (3 μm) film to polyethylene (PE), dried for 2 min at 80°C, and allowed to cure in a roll. Full cure was achieved at 23°C, room temperature, after 15 days or could be accelerated by storage at moderately elevated temperature (see Figure 5.13) [83]. The peel resistance decreased linearly with NCO consumption and was independent of temperature (see Figure 5.14) [83].

Figure 5.15 [83] illustrates the effect of variable coating storage time at 23°C (either 2 or 95 days) prior to bonding to stainless steel (SS). The bonded test specimens were kept at 65°C and peel resistance was measured as a function of the ensuing contact time. A2 represents an uncross-linked sample stored for 2 days before bonding, whereas C2 and C95 represent samples containing 3 pphr cross-linker stored for 2 and 95 days, respectively, after coating and prior to bonding. It is evident from Figure 5.15 that when bonds were formed before completion of cure, a higher ultimate peel resistance was achieved. The authors attributed this to improved substrate wetting. This may be one explanatory factor, but a later study [84] examined depth profiles and reported preferential segregation of isocyanate during cure at the steel interface. This may also have contributed to the higher equilibrium peel resistance seen in Figure 5.15 [83]. Clearly, it is important that cure should be complete before bond formation if consistent product performance is to be achieved. It is not uncommon to store coated material at elevated temperature and humidity to accelerate the cure. Amines are formed in the presence of water, which then further reacts to create urea linkages. Being more nucleophilic than the hydroxyl

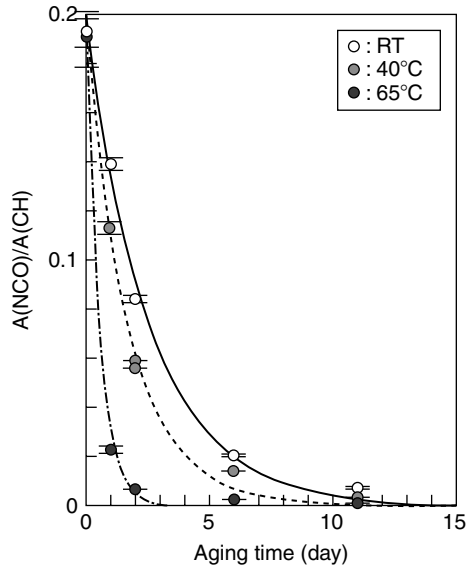


FIGURE 5.13 Plot of the IR absorbance ratio A(NCO)/A(CH) as a function of the aging time. (Reprinted from Asahara, J. et al., *J. Appl. Polym. Sci.*, 87(9), 1497, 2003. With permission.)

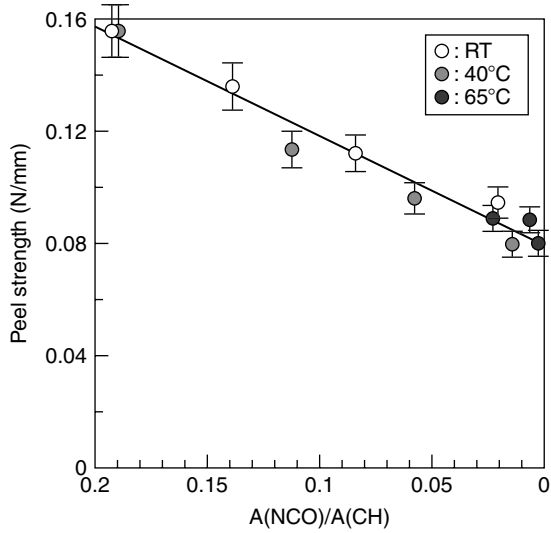


FIGURE 5.14 Plot of the peel strength versus IR absorbance ratio A(NCO)/A(CH). (Reprinted from Asahara, J. et al., *J. Appl. Polym. Sci.*, 87(9), 1497, 2003. With permission.)

groups, the amines react much more rapidly. Asahara et al. [85] compared the cure at 20°C, 0 and 79% relative humidity (RH), measuring the formation of both urethane and urea linkages. They reported that in the absence of ambient water vapor the time to fully consume the isocyanate groups increased from 20 to 120 days.

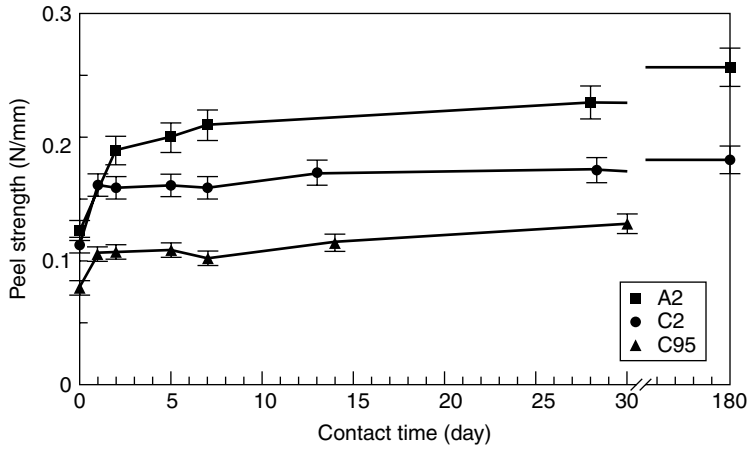


FIGURE 5.15 Plot of the peel strength as a function of the bond contact time. (Reprinted from Asahara, J. et al., *J. Appl. Polym. Sci*., 87(9), 1499, 2003. With permission.)

5.3.2.4.2 Amino Resins

These are a large class of condensation products of carbonyl-containing compounds with amines, imines, or amides. Most important are those formed by reacting formaldehyde with urea or melamine. The methylol groups thus formed may be partially or fully etherified by further condensation with an alcohol, typically butanol, to modify the functionality and solubility. They are most useful in cross-linking hydroxyl functional PSAs. Czech [27, pp. 35–38] noted that because the rate of reaction is negligible at room temperature, cross-linking is entirely controlled by a high-temperature drying step (at temperatures of 105–150°C) and can thus be precisely controlled without concern for further advancement of cure during later storage. Cross-linking can be accelerated by use of an acid catalyst, but this may not be necessary when using partially alkylated or high-imino-content melamine–fomaldehyde resins [27], the acidity of the PSA being sufficient. Indeed, Horn and Capone [86] reported that hydroxyl functional polymers could be cross-linked effectively without added catalyst by heating for 3 min at 150°C to create solvent-resistant PSAs. The best results were obtained with *N*,*N*′,*N*″-tris(dimethoxymethyl) melamine.

5.3.2.4.3 Polyfunctional Aziridines

Polyfunctional aziridines are useful in cross-linking waterborne PSAs where, under basic conditions, they provide good pot life and rapid cure upon drying. Difunctional types are sometimes referred to as "bis-amides." Although ethylene imine may be used, the reactive group is normally derived from propylene imine. Cross-linking proceeds via a ring opening addition to carboxylic acid functional groups on the polymer. In an example of this use, Iovine et al. [87] employed trimethylol-tris-(*N*-methylaziridinyl)propionate available, for example, as Neocryl® CX-100 from DSM NeoResins, Wilmington, Massachusetts, to cross-link a colloid-stabilized emulsion PSA. Czech [88] reviewed cross-linking of waterborne PSAs and included a comparison of several commercially available polyfunctional

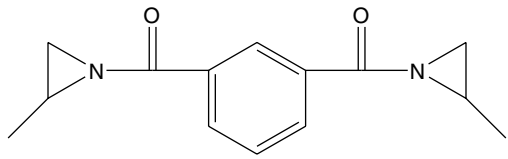


FIGURE 5.16 *N,N′*-bis-propyleneisophthalamide.

aziridines, concluding that CX-100 was the most effective, used at 0.15% w/w. Czech also compared a number of polyaziridines for suitability in cross-linking solvent-borne PSAs [89,90]. In these systems a pot life of only a few hours could be extended up to 11–12 days without detriment to the properties by the addition of a 5 wt % amine stabilizer such as triethylamine. The peel resistance, tack, and shear resistance were predictably influenced by the size and rigidity of the cross-linking molecule, with the best balance of properties being given by *N,N′*-bis-propyleneisophthalamide (BPI) illustrated in Figure 5.16, which, unfortunately, does not appear to be commercially available.

The synthesis of bis-amides was described by Watkins and McCurdy [91] and discussed in a review of a large number of polyaziridines for potential use in PSAs by Milker and Czech [92]. The use of BPI has been mentioned in several patents; for example, Kealy and Zenk used BPI to cross-link a tackified acrylic PSA and obtain excellent balance of properties including shear at 70°C, as well as good adhesion to low-energy surfaces [93]. Wilson et al. [94] used BPI to cross-link a topologically microstructured PSA surface for repositionability. Calhoun and Delgado [95] used BPI to cross-link a thermomorphic PSA containing crystalline and elastomeric phases, which enabled bonding or debonding to occur on demand by the application of moderate heat.

5.3.2.4.4 Other External Cross-Linkers

A number of other chemical reactions have been employed, most only of historical interest today. For example, the use of peroxides might be mentioned. Ulrich [96] added 1.5 wt % benzoyl peroxide to an acrylic PSA and heated the coating for 15 min at 104°C to obtain a solvent-resistant coating. He considered this time and temperature as "not greatly exceeding the usual requirement for simply drying a coating," thus enabling a single-step process! The idea of cross-linking by a free radical-induced process is, however, of great relevance today as interest grows in the use of radiation, especially ultraviolet (UV) light, to cross-link PSAs. This process will be discussed next.

5.3.3 Radiation-Induced Cross-Linking

Although polymerization of a monomer syrup directly on a coated web (discussed in Section 5.4.4) has proved to be a viable production process capable of producing tapes with outstanding adhesive performance, it is not a technology that easily lends itself to widespread adoption (see also Chapters 1 and 8). A major step forward in making UV-curing technology accessible to the larger market for coater-ready or easily formulated PSAs was the introduction by the BASF Company of a viable technology for UV-curable acrylic hot-melt adhesives. The hot-melt adhesives are prepared by conventional solution polymerization to a moderately low molecular weight (*K* value ~30–50) and

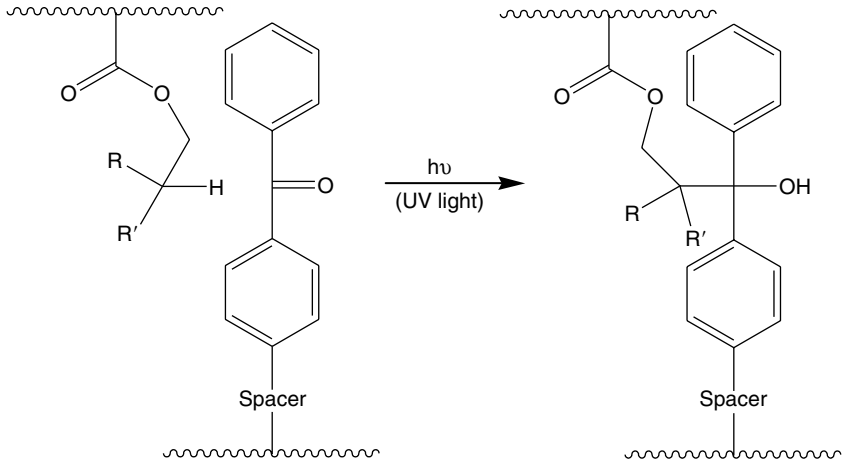


FIGURE 5.17 Mechanism of UV light-induced cross-linking.

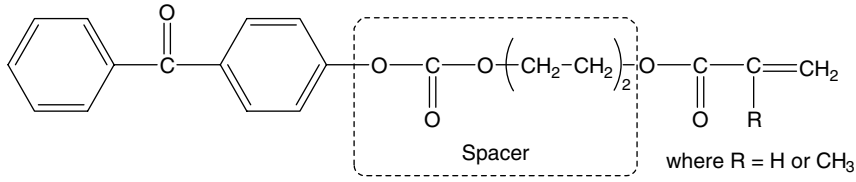


FIGURE 5.18 Polymerizable photoinitiator with spacer unit.

vacuum stripped (see discussion in Section 5.4.5.2). A benzophenone derivative photoinitiator is copolymerized into the acrylic backbone. Upon absorbing a photon of UV light, the benzophenone is excited from the singlet ground state S_0 to the S_1 state and then undergoes intersystem crossing to the T_1 triplet state, which is capable of hydrogen abstraction. Tertiary hydrogen atoms are most readily abstracted. These are available on the polymer backbone, α to the carbonyl, and at side-chain branch points, for example, in 2-EHA. The proposed cross-linking mechanism is illustrated in the Figure 5.17.

The benefits of using a built-in initiator are twofold: a cross-link is created in a single step following generation of the free radical, thus improving efficiency versus an unattached photoinitiator. Second, there is no photoinitiator that can be extracted and, by choosing a Norrish Type II initiator, there are no extractable cleavage by-products. Thus, the adhesives are suitable, for example, for medical applications. The preferred photoinitiators [97] are benzophenone derivatives with a carbonate group ortho or para to a phenyl ring. A wide variety of spacer units have been disclosed. One described as being of particular interest is illustrated in the photoinitiating monomer depicted in Figure 5.18. The spacer has proven to be the key feature in providing the necessary mobility for intermolecular cross-linking. This technology has been discussed in more detail by Meyer-Roscher et al. [98].

5.4 Synthesis

PSAs are typically produced in a stirred tank reactor equipped with a jacket for heating and cooling, a condenser, and a number of auxiliary tanks equipped with meters for the addition of monomers, initiator, and any other required components for the particular process. Quite frequently, the polymerized product is a "base" polymer emulsion or solution that is then transferred to another stirred tank for formulation with additional components such as a tackifiying resin, cross-linker, or diluent (see also Chapter 8) and adjustment of the final solids content and viscosity, as desired for subsequent coating. The final product is then filtered and transferred to bulk containers or packaged into drums (see also Chapter 10).

5.4.1 Free Radical Addition Reaction Mechanism

The steps involved in homogeneous free radical polymerization are illustrated in Figure 5.19 for the most common case where the initiator dissociates into two free radicals. These equations can, of course, be generalized to describe the kinetics of copolymerization [99].

Initiation is achieved in one of two ways: by homolytic dissociation, using heat or UV light, or by a redox reaction. Two well-known examples of thermal initiators used in solution polymerization are illustrated in Figure 5.20 (for thermal and redox initiators used in emulsion polymerization see Section 5.4.3.2.1). Note that the primary radical must further react with a monomer to begin the polymerization process. A significant fraction of primary radicals are often lost to formation of by-products.

The sequential addition of monomer to initiating radicals (chain propagation) proceeds immediately to build a high-molecular-weight polymer, even in the early stages when most of the monomer remains unreacted. The typical propagation reaction is depicted in Figure 5.19.

Termination of growth usually arises from two polymer radical chain ends coming together to combine or to disproportionate, as illustrated in Figure 5.19. Which reaction path is dominant depends upon the particulars of the monomers and polymerization conditions, with less hindered radicals such as methyl acrylate or acrylonitrile

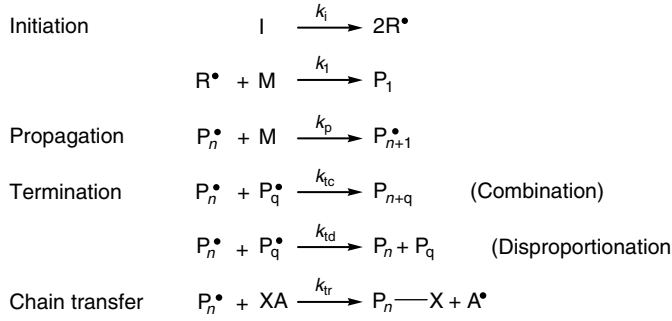


FIGURE 5.19 Reaction steps involved in free radical polymerization.

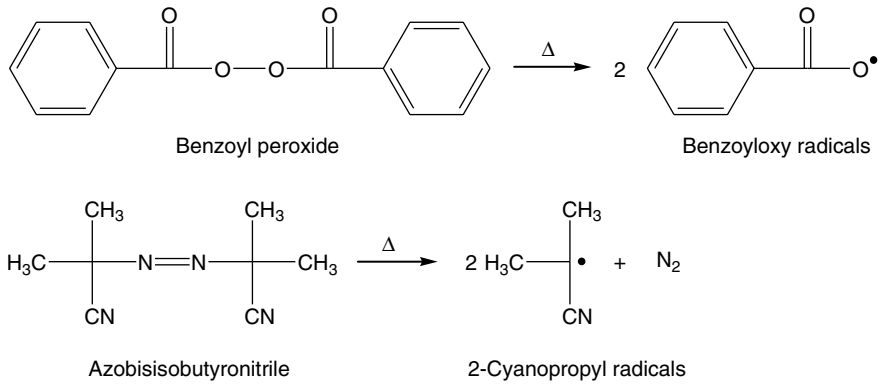


FIGURE 5.20 Examples of thermal initiators used in solution polymerization.

tending to combine, whereas MMA has a greater propensity for disproportionation [100, pp. 242–243].

Chain transfer, also known as radical displacement, refers to the premature termination of a growing polymer chain by reaction with another molecule to create a dead polymer molecule. However, as distinct from the termination reactions discussed above, which consume radicals, in chain transfer reactions a new radical is generated. This, in turn, reacts with a monomer to initiate polymerization of a new chain. All components present in the reaction are capable of acting as chain transfer agents: initiator, monomer, solvent, and polymer, as well as CTAs, which may be added specifically for this purpose. The effect is thus to reduce molecular weight while preserving the number of radicals. (An exception arises in transfer to polymer, where the degree of polymerization is not necessarily decreased [100]. This is discussed in Section 5.3.2.1.1.) Provided that the rate of reinitiation is comparable to the rate of propagation, k_p, the rate of polymerization is unaffected. Although sometimes a problem, in PSA production chain transfer is often used to advantage to regulate molecular weight, particularly to improve tack.

5.4.2 Organic Solution Polymerization

The first acrylic PSAs were polymerized in organic solution. Today, the emulsion process dominates commercial production, but solution polymerization continues to be important in a number of applications where emulsion polymers have not yet fulfilled all requirements for adhesive performance and coating quality (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

In a typical production process, a portion of the monomer and solvent, sufficient to cover the agitator, is charged to the reactor, oxygen that inhibits polymerization is purged from the headspace with an inert gas such as nitrogen, and jacket heating is begun. At this point, initiator may or may not be present. Because heating times may be variable, there can be some advantage to delaying the introduction of initiator until the reaction temperature is reached, provided that it can be quickly and

uniformly incorporated. Once the mixture begins to reflux and initiator is present, the reaction proceeds rapidly. The reaction is exothermic and the heat of polymerization is removed by the vaporization and condensation of solvent and the more volatile monomers. Jacket heating is adjusted to maintain a controlled reflux throughout the reaction. Note that by operating under reflux conditions, the reaction temperature is entirely controlled by the boiling point of the mixture in the reactor, which results in a very reproducible process from batch to batch. After a short interval, further addition of monomer, solvent, and initiator begins and continues for several hours at controlled rates until all the reactants and polymerization solvent have been added to the reactor. After an additional period under reflux to complete the reaction, the polymer solution is ready to be diluted, cooled, and discharged from the reaction vessel.

5.4.2.1 Process Control of Molecular Weight

There are several process variables that are commonly employed to control and alter molecular weight as needed. These are reaction temperature, monomer concentration, initiator choice and concentration, and the use of chain transfer agents. Applying the steady state approximation, which assumes that the concentration of radicals remains constant after an initial rapid increase, to the reactions in Figure 5.19 and ignoring chain transfer, the following equation for the kinetic chain length, ν, can be derived [100],

$$\nu = \frac{k_p[M]}{2(fk_dk_t[I])^{1/2}} \tag{5.2}$$

where f is an initiation efficiency factor. In the limiting cases of termination solely by combination, the number average degree of polymerization is $\overline{X}_n = 2\nu$, and in the case of termination solely by disproportionation, $\overline{X}_n = \nu$. The number average molecular weight, M_n, is given by $M_n = M_0\,\overline{X}_n$, where M_0 is the monomer molecular weight.

This is a simple model for a homopolymerization, but demonstrates the key point that the molecular weight increases with monomer concentration and varies inversely with the square root of initiator concentration. The effect of a change in temperature is less obvious because three rate constants are involved and must be assessed collectively [100, pp. 275–278]. Normally, an *increase* in the reaction temperature results in an increased rate of polymerization and *reduced* molecular weight.

Initiators are selected to have a decomposition half-life appropriate to the reaction temperature, as well as to be soluble in the monomer–solvent mixture. Azo initiators such as azo-bis(isobutyronitrile) or an organic peroxide such as dilauroyl peroxide or *t*-butyl peroctoate are typical. Dibenzoyl peroxide is less commonly used today because benzene is produced as a toxic by-product. For a given initiator, the rate of decomposition depends strongly upon the temperature, which, in turn, can be controlled by the choice of a polymerization solvent with a greater or lesser boiling point. Ethyl acetate, bp 77°C, is a common choice of solvent. For cost reduction or to change the reflux temperature, it is common to use a mixture of ethyl acetate with a hydrocarbon solvent such as a mixed isomer technical grade of hexane or heptane. Combination with a lower boiling point solvent such as hexane or acetone will raise the molecular weight

TABLE 5.2 Monomer Chain Transfer Constants

Monomer	$C_M \times 10^4$
Methyl acrylate	0.036–0.325
Ethyl acrylate	1.25
n-Butyl acrylate	0.373–1.25
2-Ethylhexyl acrylate	6.28,[a] 3.79[b]
Methyl methacrylate	0.07–0.18
Vinyl acetate	1.75–2.8
Acrylonitrile	0.26–1.02
Styrene	0.07–1.37

Temperature was 60°C except as noted: [a]70°C; [b]80°C.
Source: Data from Brandrup, J., et al., Eds. (1999). *Polymer Handbook*, 4th ed., John Wiley & Sons, New York. With permission.

TABLE 5.3 Chain Transfer Constants for Solvents

	$C_s \times 10^4$ for Polymerization of				
Solvent	Methyl Acrylate	Ethyl Acrylate	2-Ethylhexyl Acrylate	Methyl Methacrylate	Vinyl Acetate
Ethyl acetate	—	0.89	—	0.240	7.8[a]
Acetone	0.62–1.1	—	—	0.225–0.275	42[b]
n-Hexane	—	0.59	—	—	—
Cyclohexane	—	1.22	—	0.10	6.59, 7.0, 100
Toluene	—	2.60	2.13	0.292–0.525	91.6
Isopropanol	—	28.7	—	1.907	44.6[a]

Temperature was 80°C except as noted: [a]70°C; [b]75°C.
Source: Data from Brandrup, J., et al., Eds. (1999). *Polymer Handbook*, 4th ed., John Wiley & Sons, New York. With permission.

(see also Chapter 8). However, solvent boiling point is not the only consideration. The chain transfer characteristics of the solvent can play a critical role. Thus, solvents such as toluene with a moderately high chain transfer constant, defined as $C = k_{tr}/k_p$, reduce the molecular weight. Solvents with a high chain transfer constant such as isopropanol are to be avoided and, if required for cross-linker stabilization, for example, are added postpolymerization, preferably in a separate vessel.

Chain transfer constants for some important monomers are listed in Table 5.2 [101] and for solvents in Table 5.3. VAc and 2-EHA have the highest rates of chain transfer to monomer among these common monomers. Among the solvents, there is some variability in the literature values due to differing conditions for measurement. However, in the polymerization of acrylate monomers, chain transfer to toluene and especially isopropanol rank highest, as noted above. This is also true for polymerization of VAc, but chain transfer to solvent in general, even ethyl acetate, is significantly higher in the case of VAc than for the other monomers. These values of chain transfer constant are sufficiently high to have a large impact on the PSA properties due to the relatively high molar concentrations in which these monomers and solvents are used. However, to put

the numbers in a proper perspective, one should note that values for mercaptan CTAs exceed these by a factor of 10^4 to 10^5.

The most useful method to adjust molecular weight during process scale-up without causing a change in the overall composition is to adjust the instantaneous monomer concentration by redistribution of the monomer and solvent between the initial charge and the slow feeds or by changing the monomer feed rate. A less common approach is to adjust the reflux temperature by the application of pressure or vacuum. This, of course, is only possible in reactors that are designed to withstand it.

5.4.3 Emulsion Polymerization

Unlike solution polymerization, which is homogeneous, emulsion polymerization is heterogeneous. The reaction takes place within the growing particle, as well as in the continuous aqueous phase or serum, as it is sometimes called. Consequently, it is a much more complex process. In addition to water, monomers, and initiator, the starting materials include emulsifiers and, optionally, buffers, CTAs, and perhaps seed latex. In a typical process, the emulsifier is dissolved in water at a concentration above the critical micelle concentration (CMC). The monomer is introduced into this solution with agitation to form an oil-in-water emulsion. The particle size of these monomer droplets is typically in the range of 1–10 μm. A small fraction of the hydrophobic monomer is dissolved in the aqueous phase. The process plays a major role in determining the adhesive properties, as well as the latex physical properties, and so a short description of the major features will now be given.

5.4.3.1 Emulsion Polymerization Models

It is common to describe the batch reaction process in terms of the three stages proposed by Harkins [102], later quantified, first by Smith and Ewart [103], and further refined by many others. In this qualitative description the locus for initiation of a polymer particle resides in micelles formed by the very small amount of monomer, which is dissolved in the continuous aqueous phase and surrounded by a monolayer of anionic surfactant. Normally, a water soluble initiator is used. An initiating free radical diffuses into the monomer swollen micelle and starts the polymerization process. The monomer swollen micelles, of size 10–20 nm, have a large collective surface area compared with the monomer droplets; hence, the probability of a free radical entering a droplet is small. As the monomer is consumed in the growing particle, a concentration gradient drives diffusion from the reservoir of monomer droplets and monomer swollen micelles to the particle. The particles are assumed to grow until another free radical enters to terminate the reaction. Growth resumes when a new free radical enters the particle. This first stage involving particle nucleation is considered complete when uninitiated micelles are no longer present and no new particles are formed. About 10–15% of the monomer has normally been converted at this stage.

In the second stage, polymerization proceeds within the swollen particles until all the monomer in the droplets has been consumed, at which point the conversion is typically about 40–60%. During this stage, the particle size increases but the number of particles remains constant. Because the rate of reaction is proportional to the monomer

concentration, the reaction proceeds more rapidly than in a homogeneous solution polymerization. During the third stage, the monomer within the particles is converted to polymer. The rate of reaction decreases as the monomer concentration is now decreasing. During this stage, chain transfer to polymer resulting in branching and intraparticle cross-linking becomes increasingly probable. CTAs may be used to mitigate this effect if adhesion properties and tack are adversely affected.

This model, although useful, should not be viewed as a complete descriptor of the emulsion polymerization mechanism and many investigators have elaborated upon the model. Harkins noted in his original paper that a secondary locus of initiation is the aqueous phase, which becomes more important as the concentration of the emulsifier is decreased. Polymerization can be initiated below the CMC or even in the absence of emulsifier. It has been proposed [104] that water-soluble oligomers formed by aqueous phase initiation become insoluble with increasing chain length and create small particles in a process of homogeneous nucleation. Monomers with appreciable water solubility such as VAc, MA, acrylonitrile, or acrylamide, to name a few, may further complicate the picture by forming polymer in the continuous as well as the dispersed phase.

Coalescence, initially between micelles and particles and later between particles, is particularly important in determining the particle size distribution and stability of an emulsion under an applied shear stress. Coalescence is affected by the size and surface charge density of the particles, as well as the degree of agitation. Nomura [105] demonstrated that higher agitation increases the particle size distribution. The polymerization kinetics are also affected by shear-induced reduction of monomer droplet size, which reduces the aqueous emulsifier concentration and the number of micelles and increases monomer diffusion out of the droplet. One practical consequence is that emulsion PSA polymerization, in comparison with homogeneous solution polymers, is much more sensitive to the details of reactor and agitator geometry and mixing.

A more general model by Min and Ray [106], in addition to these factors, takes into account desorption of radicals from the particle, stabilization by polymer chain ends as well as emulsifier, particle size distribution, and the possibility of nonuniform structures within the particle. Their model is applicable to semicontinuous as well as batch reactions. In industrial practice, emulsion PSA production typically begins with an initial charge to the reactor of emulsified monomer or a polymerized seed latex. The process then proceeds with a continuous emulsion feed. This allows much better control of the reaction compared with a batch process. Clearly, many variants are possible to exercise additional control of the particle morphology by phased introduction of selected monomers.

5.4.3.2 Materials Selection for Emulsion Polymerization

In comparison with an organic solution polymerization, emulsion polymerization requires a number of additional components. In addition to water, monomers, and an initiator, stabilizers, CTAs, and buffers are typical components.

5.4.3.2.1 Initiators

Free radicals are produced by thermal decomposition of peroxy compounds or via redox reactions and in the production of emulsion PSAs are normally water soluble, in contrast

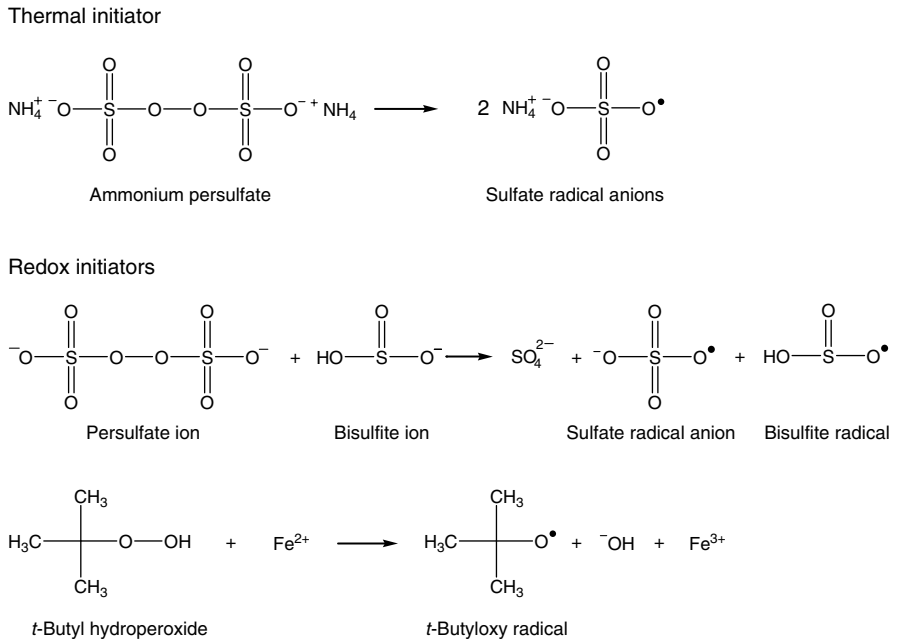


FIGURE 5.21 Examples of initiators used in emulsion polymerization.

with the oil-soluble initiators employed in organic solution polymerization. Examples are illustrated in Figure 5.21. The most widely used thermal initiators are sodium, potassium, or ammonium persulfates, which dissociate into two sulfate radical anions. It is common to use a buffer such as sodium bicarbonate to prevent acid-catalyzed decomposition of the persulfate, which does not yield free radicals. Typical redox couples include a persulfate used with a reducing agent such as a bisulfite or iron(II) compound, as well as sodium formaldehyde sulfoxylate, in combination with an oxidizing agent such as *t*-butyl hydroperoxide. These are useful at low temperatures.

5.4.3.2.2 Stabilizers

As described above, the function of the stabilizers is to establish particle nucleation and to stabilize the particles against flocculation. Much work has been devoted to countering the generally detrimental effects of these stabilizers on adhesive properties and especially on water and humidity resistance. In addition to the surfactants and emulsifiers discussed below, it should be noted that initiator fragments and, when employed, hydrophilic carboxylic acid comonomers such as acrylic acid contribute to particle stabilization. The acidic monomer is a main component of water-soluble chains adsorbed on the particle surface and provides electrostatic as well as steric stabilization. This electrosteric stabilization has been investigated in detail by Vorwerg and Gilbert [107].

Anionic and Nonionic Surfactants Anionic surfactants are the most commonly encountered stabilizers. Electrostatic stabilization and pH-dependent behavior are determined

by the hydrophilic head group, whereas the hydrophobic chain influences adsorption and steric stabilization of the latex particle, interfacial tension, and the CMC. One important class are the salts of sulfonic and fatty acids, for example, sodium dodecyl sulfate (SDS), which has been widely studied. Other common examples include sodium dihexyl and dioctyl sulfosuccinate. Ammonium salts are also useful and may promote improved water resistance by loss of ammonia upon drying. Phosphate esters, among many other types, are also used.

Nonionic surfactants tend to aggregate at higher temperatures and therefore tend not to be effective stabilizers when used alone unless polymerization is carried out at low temperature. They are, however, frequently used in combination with anionic surfactants. Polyethoxylates of octyl and nonyl phenol have been widely used but are under environmental scrutiny as reputed endocrine disruptors. Other common classes include the polyethoxylates of straight chain alcohols and block copolymers of ethylene oxide (EO) and propylene oxide (PO) such as the triblock PEO–PPO–PEO and tetrafunctional block copolymers formed by the sequential addition of PO and EO to ethylene diamine.

Polymeric Emulsifiers Polymeric emulsifiers, also called protective colloids, function by creating entropic (steric) repulsion between particles. An example is poly(vinyl alcohol) (PVOH), which, used alone or in combination with anionic surfactants, is widely used to stabilize homopolymers and copolymers of VAc for wet bonding applications, where it contributes to wet tack. PVOH is not generally effective in stabilizing acrylic emulsions due, it is believed, to an inability of the monomers to graft to the colloid. Yuki et al. [108] were able to use PVOH with a thiol end group to prepare stable emulsion copolymers of BA with MMA. However, despite having a T_g of −30°C for a 70/30 w/w ratio, Young's modulus increased by almost an order of magnitude compared with an emulsion stabilized by anionic surfactants and well above Dahlquist's criterion for pressure-sensitive properties. The authors attributed this to crystallinity within the PVOH.

Park and Lee [109] prepared a series of low-molecular-weight, high-acid copolymers of 2-EHA, BA, and AA for use as polymeric emulsifiers. When neutralized with KOH and used to prepare emulsion PSAs from 2-EHA and BA, the resulting average particle size was ~150 nm and most exhibited excellent freeze–thaw stability. Balanced adhesive properties could be obtained by controlling the emulsifier molecular weight and acid number. Iovine et al. [87] used low T_g copolymers of 2-EHA, AA, and PEG methacrylate as protective colloids to prepare emulsion PSAs. These were capable of being coated on a silicone release liner without added thickeners to yield a solution-like coating quality.

Polymerizable Surfactants (also known as reactive surfactants) Ethylenically unsaturated emulsifiers that can be copolymerized with the adhesive monomers are used to overcome the problem of surfactant migration by covalent bonding to the polymer. Numerous benefits have been demonstrated to accrue from eliminating surfactant mobility, including improvements in interfacial peel resistance, water resistance (see also Chapter 8), mechanical stability under conditions of high shear, freeze–thaw stability, and electrolyte tolerance.

Typically, the surfactant is incorporated in the chain propagating step, in which case it may be referred to as a *surfmer*. Among a number of useful reviews of reactive

surfactants in emulsion polymerization are those by Guyot and Tauer [110] and Asua and Schoonbrood [111]. A number of examples of use in PSAs exist in the patent literature. Representative of these is the disclosure of Howes [112], who used sodium monolauryl itaconoxypropane sulfonate to prepare an emulsion PSA for use in a surgical or medical dressing.

A common difficulty in using a reactive surfactant is the loss of stabilization attributable either to burial of the surfactant within the particle, if too reactive and consumed early, or to reaction in the aqueous phase, creating water-soluble oligomers. These may adsorb on neighboring particles, causing bridging flocculation [111]. The formation of water-soluble surfactant oligomers can be avoided by the use of maleate diester surfactants, which, due to their low ceiling temperature, do not homopolymerize [110]. Lu et al. [113] used, in addition to an ionic copolymerizable surfactant, a small amount, preferably 2–5%, of a low-molecular-weight hydrophobic polymer such as a polystyrene tackifying resin, to enhance emulsion stability during polymerization. This is believed to function by enabling increased surfactant absorption on the monomer droplet surfaces and by inhibiting monomer diffusion from smaller to larger droplets.

Special measures may be necessary to ensure efficient use and high conversion of the surfmer, without which the intended benefits will not be realized. For example, Amalvy et al. [114], in preparing a styrene-acrylate latex stabilized with sodium tetradecyl 3-sulfopropyl maleate, introduced VAc and vinyl versatate at the end of polymerization to achieve high surfmer conversion.

5.4.3.2.3 Chain Transfer Agents

Although many chemicals are capable of chain transfer, mercaptans (thiols) such as DDM are most commonly employed in emulsion PSA polymerization owing to their very high chain transfer constants and therefore require only small amounts to be used, typically about 0.1% w/w of the monomer. DDM has relatively low volatility and is sufficiently able to diffuse from monomer droplets into the aqueous phase [54]. The effect of chain transfer on the gel content of emulsion PSAs was discussed in Section 5.3.2.1.1.

5.4.3.3 Effect of Chain Transfer Agent Level on Adhesive Performance

Gower and Shanks [115] conducted a systematic study of the effect of CTA level on a series of emulsion PSAs in which both the level of CTA and the ester monomer composition was varied, the latter from 0–75% EHA, fixed 4% AA, and the balance made up of BA and MMA to maintain constant T_g. As expected, the gel content decreased with increasing level of CTA, but also increased with EHA content due to increased chain transfer to polymer. As EHA increased, so too did the level of MMA to maintain constant T_g. This moderates the tendency for chain transfer, as discussed in Section 5.3.2.1.1. At high levels of gel (~60%) the adhesive performance was not greatly dependent upon composition. At lower gel levels (higher CTA) the performance was correlated with changes in polymer viscosity due to compositional variation.

The authors constructed time–temperature superposition master curves of peel resistance. In the regions of cohesive failure shift factors for polymers with high levels

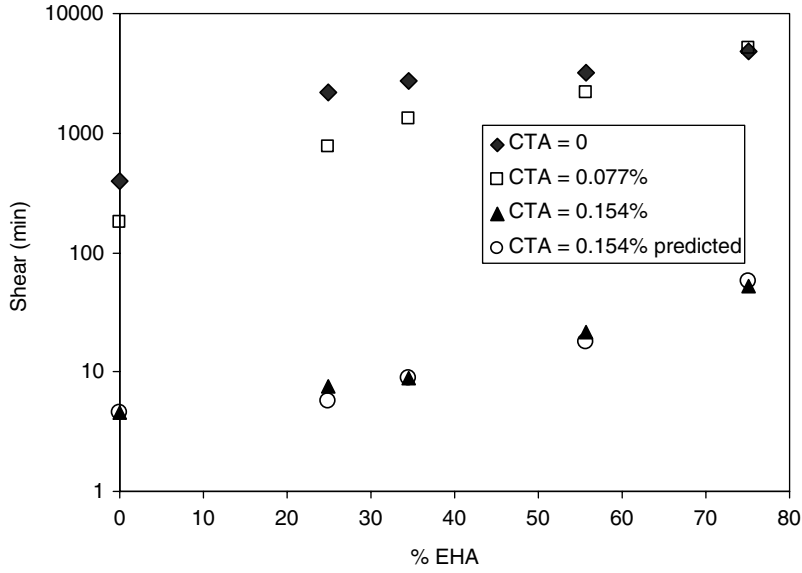


FIGURE 5.22 Static shear resistance as a function of copolymer composition and level of chain transfer agent. (Data from Gower, M.D. and Shanks, R.A., *Macromol. Chem. Phys.*, 205(16), 2139–2150, 2004.)

of CTA closely followed the Williams–Landel–Ferry equation. They were then able to create "super" master curves by shifting the cohesive regions for different compositions into superposition. Applying the compositional shift factor to the experimental reference shear value (chosen to be 0% EHA) gave an excellent prediction of static shear for the higher levels of EHA, as illustrated in Figure 5.22.

5.4.3.4 Miniemulsions

In a miniemulsion polymerization the reaction mixture is sonicated with high energy to reduce the monomer droplet size to 50–500 nm. Stabilization is achieved with an emulsifier, used below the CMC to avoid micellar nucleation, in combination with a hydrophobic cosurfactant such as a long-chain alkane. A hydrophobic comonomer such as stearyl methacrylate can also serve this purpose. A number of benefits have been cited for the miniemulsion process. One benefit is that particle size can be controlled by the intensity and duration of sonication. There is little subsequent mass transfer between particles due to the low water solubility of the cosurfactant. Hence, the size distribution can be maintained throughout the process. The rate of monomer conversion is much more rapid than in conventional (macro)emulsion polymerization. A further advantage is that the miniemulsion process affords the possibility of more control over molecular weight distribution. A detailed review of miniemulsion polymerization has been given by Asua [116].

Bunker et al. [117] employed the miniemulsion technique to prepare a PSA from acrylated methyl oleate, a highly water-insoluble monomer derived from renewable plant oil.

Excessive amounts of surfactant and long reaction time are required to polymerize this monomer by a conventional emulsion process.

Jovanovic et al. [118] compared seeded emulsion polymerizations of BA/MMA prepared by conventional and miniemulsion processes with the objective of generating a second particle population with smaller size and lower molecular weight. To achieve this, they prepared conventional and miniemulsion seed latices followed by conventional slow feeding of emulsified monomer and finally a rapid feed of either pre-emulsified monomer or a miniemulsion mixture. The hybrid miniemulsion process yielded bimodal particle size distribution, in addition to a bimodal distribution of molecular weight and gave a substantial improvement in rolling ball tack (as expected for bimodal MW) at comparable peel and shear resistance. Not unexpectedly for a composition lacking functional monomer, shear strengths were low but the work demonstrates the control of physical properties that is possible using miniemulsions.

5.4.3.5 High-Solids Emulsions

High-solids emulsions, by which we mean emulsions with a solids content of at least 65% (corresponding, for a typical acrylic, to a polymer volume fraction above 0.60) offer important economic advantages in reduced transport and packaging costs and also in the energy required for drying. A random close packing of uniform noninteracting hard spheres occupies a volume fraction of about 0.64. As a monodisperse latex approaches this limit, the viscosity rises dramatically and because the particles interact it is increasingly difficult to achieve stability. The solution to achieving high solids and low viscosity is to pack smaller particles between the large ones. Bimodal and trimodal particle size distributions have been used.

Miniemulsions often produce a broad particle size distribution and have therefore been investigated for high solids. For example, Unzué and Asua [119] prepared a BA/MMA/VAc terpolymer at 65% solids with viscosity of 440 mPa · s. However, the need for specialized equipment to reduce droplet size makes this method less attractive for industrial production when conventional emulsion polymerization methods can be adapted to the task. Because some water-soluble monomer is always present, careful attention must be paid to controlling and limiting homogeneous nucleation, which, if uncontrolled, will raise the viscosity and consume surfactant. Much of the published work on producing multimodal high-solids emulsions resides in the patent literature. One method is to mix two or more preformed monomodal seed latices and continue growth in a semibatch process. Another is to begin with a seed latex, continue growth in a semibatch reaction, and then nucleate a secondary population and perhaps a third. Maintaining control of the evolving particle size distribution is the key. In a series of three papers, McKenna and coworkers [120–122] have studied the relationship among particle size distribution, solids content, and viscosity, dissected the patent literature, and discussed in detail the preparation of seed latices and high-solids emulsions using a BA/MMA/AA composition as a model PSA. Using this conventional approach they were able to achieve solids content above 65% (w/w) and viscosity below 2500 mPa · s. In a fourth paper [123], they proposed an improved strategy. Using the same model PSA composition they preswelled a large particle size seed with an oil-soluble initiator instead of the usual water-soluble one. This avoided the problems of homogeneous

nucleation and gave excellent control of particle size distribution. The lowest viscosity was obtained with a bimodal latex of 85% (v/v) large particles (900 nm) and 15% small (110 nm). No advantage was obtained using a trimodal distribution. Residual monomer was treated with a water-soluble redox couple. The resulting emulsions had solids content of 73% and viscosity between 300 and 1000 mPa · s. In addition, water uptake of the dried film and sensitivity of latex viscosity to change in pH was reduced compared with products made by the standard technique.

5.4.4 Radiation-Initiated Free Radical Polymerization

Radiation-initiated polymerization of PSAs is the least widely practiced method but has many attractive features. Foremost, it eliminates the need for solvents or water as a vehicle for polymerization and coating, thus eliminating the need for costly drying ovens, the space and energy to operate them and, in the case of solvents, the need to incinerate or recover the waste stream. The ability to polymerize the monomers *in situ* as a thin film on either the backing substrate or the release liner avoids the normal difficulty of maintaining thermal control and mixing when attempting a bulk free radical chain polymerization (see also Chapter 1).

A further benefit of polymerizing directly on the coated web is that it becomes possible to incorporate large amounts of polar functional monomer, such as AA and acrylamide, without encountering the problems of high solution or melt viscosity or, in the case of emulsions, loss of tack and poor water resistance due to polymerization in the aqueous phase.

Electron beam (EB) and UV light are both used to initiate the process, but EB needs a much higher capital investment (see also Chapter 8). On the positive side, it can penetrate opaque materials, if necessary, and requires no costly photoinitiator, but unless the economics of scale can justify the investment UV is likely to be the method of choice. It is particularly well suited to narrow web graphics applications, where the adhesive is applied and polymerized on a printing press but is not entirely limited in commercial practice to these small-scale applications. Blanketing the coating with an inert gas such as nitrogen is a necessity with EB to prevent ozone formation but is also preferred with UV to prevent inhibition of polymerization at the surface by oxygen (see also Chapter 10).

5.4.4.1 Monomer Blends

Conceptually, the simplest approach is to apply the desired mixture of monomers to the substrate and initiate polymerization. This technique was described by Fukukawa et al. [124], who subjected a 50-μm coating of monomers to a 50-kGy electron beam dose from a 300-kV source. In addition to excellent adhesive properties, they noted that the technique provided good anchorage of the adhesive to olefinic films. The method, however, suffers from two significant drawbacks: the conventional monomer mixture is very low viscosity and it is toxic. It is therefore difficult to coat at the desired thicknesses. Polymerization on a coated web instead of within a reactor obviously calls for additional attention to chemical hygiene. This is an issue with all variants on this method, as opposed to radiation-induced cross-linking of an already formed polymer (discussed in Section 5.3.3).

5.4.4.2 Monomer Syrups

This term is applied to solutions of polymers or oligomers in monomer (see also Chapter 1). The increase in viscosity solves the coating problem and a great variety of formulations are possible to address the varied requirements of adhesive performance. Fukukawa et al. [124] suggested using a tackifier, but many polymers, including elastomers, have subsequently been investigated. There has also been considerable work to find suitable monomers with lower volatility and toxicity but generally at higher cost and some sacrifice in adhesive performance. A review has been given by Huber [125] and numerous examples exist in the patent literature.

One reason for the often modest adhesive performance of monomer syrups is that, to achieve high production line speed, polymerization is initiated with a high dose of short-wavelength UV light, resulting in low molecular weight. The addition of multifunctional monomers in compensation results in higher-than-desirable cross-link density. This problem was addressed in an important innovation by Martens et al. [126]. After first polymerizing a monomer mixture to about 10% conversion, preferably by UV-induced photopolymerization, they irradiated the syrup using a bank of 24 cylindrical fluorescent blacklight lamps. This low-intensity, long-wavelength UV light enabled them to control and limit the rate of polymerization. The UV source, when operated at normal voltage, produced a light intensity of about 0.3 mW/cm^2, confined almost entirely to the wavelength range of 320–380 nm. The best results were obtained when photoinitiator concentration and line speed were adjusted to achieve full (i.e., >95%) conversion with about 3–5 min of UV exposure. They demonstrated that long-wavelength UV is essential to achieving high cohesion; short-wavelength UV sources, even when used at comparable intensity and with a reduction of photoinitiator concentration to achieve similar rates of polymerization (because the chosen photoinitiator had much higher quantum yield for initiation at short wave length), resulted in polymers with very low cohesion. Wavelengths in the infrared region (>800 nm) were also detrimental to properties due to heating; polymerization temperatures below 35°C were necessary for good results. This long-wavelength UV technique achieves high molecular weight and consequently a good balance of shear holding power and peel resistance. Addition of a photocross-linker gave very high cohesive strength while maintaining good peel.

5.4.5 Reduction of Residual Monomers

Unless special steps are taken, a solution acrylic polymerization will normally proceed to about 95–97% monomer conversion. Most objectionable are the low-volatility higher acrylates such as 2-ethylhexy or *iso*-octyl acrylate, which are difficult to remove when drying the coated adhesive and remain in the finished product, creating an odor. In skin-contacting applications there may also be concern regarding the potential for sensitization. In transdermal patches there is the additional complication of potential chemical interactions with the active ingredient. When a less reactive comonomer such as VAc is present, the acrylate monomers are preferentially reacted and no additional steps may be necessary to achieve a low-odor coating because the boiling point of VAc is just 73°C and is easily removed in a drying oven.

5.4.5.1 Organic Solutions

5.4.5.1.1 Scavenging Initiators and Monomers

With a late addition of a short-halflife initiator (sometimes called a scavenger) and at the cost of an extended holding time at reflux temperature, the acrylate monomers in an all-acrylic PSA solution can be reduced to below 1000 ppm, a common target. A high-molecular-weight fraction may form in the process, which can alter performance and perhaps negatively impact coating rheology. This can be minimized by judicious choice of the scavenger initiator. This technique, however, is not effective in reducing VAc, which is only minimally reduced by such a scavenging technique. As discussed, this may be unimportant in many situations. Indeed, Brown added VAc at the completion of an otherwise all-acrylic polymerization to act as a scavenging monomer for the residual acrylates [127].

5.4.5.1.2 Extraction

Extrusion of the polymer solution into a counter current of a solvent in which the polymer precipitates as fibers has been described as an effective method of removing residual monomers [128]. By extruding a solution of an *iso*-octyl acrylate/acrylamide copolymer into methanol, the residual comonomers were reduced by a factor of 295 and 850, respectively. A disadvantage of this method is that it is suggested to redissolve the precipitated high-molecular-weight PSA to produce a coating.

5.4.5.1.3 Hydrogenation

In transdermal delivery it is a common practice to mix solutions of the active ingredient and adhesive prior to coating to produce a drug-in-adhesive patch. In a case where one or more residual monomers react with the drug, it becomes necessary to eliminate the monomer as completely as possible. An effective process for accomplishing this, dubbed "reduction by reduction," is to hydrogenate the polymer solution using heterogeneous catalysis [129]. VAc is converted to ethyl acetate, which is normally already present as a solvent, the acrylates are converted to the corresponding propionates, which are also likely to be nonreactive, and so forth. This process enables the residual monomers, including VAc, to be reduced to below the analytical detection limits.

5.4.5.2 Hot Melts

A well-known method of devolatilizing polymers is to introduce a sparging gas, such as steam. By raising the partial pressure of the volatile material, the rate of evaporation is increased. This method has been applied to the devolatilization of a UV-curable acrylic hot melt produced by solution polymerization, thus reducing residual monomer and solvent to less than 0.1%. The efficiency of the process was enhanced by recirculating the molten adhesive through a side arm of the reactor to increase the exposed surface area [130].

5.4.5.3 Emulsions

In emulsion polymers conversion is much higher, typically 99% or more, but it is still desirable to reduce residual monomers for some applications. This may be

accomplished by treating the polymerized emulsion with an oil-soluble initiator [131]. Rupaner et al. [132] described a process to reduce residuals using a water-soluble redox couple initiator. Alternatively, sparging the emulsion with steam has been used and special columns have been designed for the purpose of increasing the area of the gas/emulsion interface [133].

5.5 Compounding

Although acrylic PSAs are sometimes used as polymerized, in many cases the polymer will require some additives to modify adhesive performance, to facilitate the coating process, or to improve stability during storage. Depending upon raw material supply and demand, there may be cost advantages to motivate compounding (formulating) or simply a desire to minimize inventory of polymers for single applications. The role of formulating and methods of formulation are described in Chapter 8 by Benedek.

5.5.1 Compounding to Modify Adhesive Performance

A number of performance-modifying materials are available to the formulator. Of particular importance are tackifying resins and plasticizers. Acrylic emulsion PSAs can also be blended with other polymer dispersions to improve properties. Adhesion-related formulation is also discussed in Chapter 8.

5.5.1.1 Blending Emulsion Pressure-Sensitive Adhesives

Mixing acrylic PSAs in solution is sometimes possible but not widely practiced. Particular attention must be paid to the solvent system to ensure that the polymers are compatible and do not phase separate in solution. Having the same solvent system does not guarantee compatibility if the polymers differ greatly in polarity. This problem is avoided when blending acrylic emulsions because nearly all employ anionic particle stabilization. The pH is typically adjusted with ammonia into the range ~6–8.5 before mixing (see also Chapter 8). Brooks et al. [134], hoping to improve the balance of adhesive properties by creating synergistic blends, concluded that this approach is generally not productive unless the blended species are structurally very similar, with improvements in one property resulting in unacceptable trade-off in another (for blending technology of water-borne PSAs, see Chapter 10).

5.5.1.2 Tackification

Next to cross-linking, which has already been discussed in Section 5.3, tackification is perhaps the most useful formulating tool (see also Chapter 8). The chief benefit of the addition of tackifier, which raises the entanglement molecular weight, is the improvement in adhesion to difficult-to-bond, low-surface-energy substrates such as untreated polyolefins. However, this gain in versatility of adhesion is not without penalties. These low-molecular-weight materials reduce the modulus at higher temperatures, which negatively impacts cohesive strength and creep resistance. The glass transition temperature is raised, which detracts from low-temperature bond formation; see Figure 5.23. Many

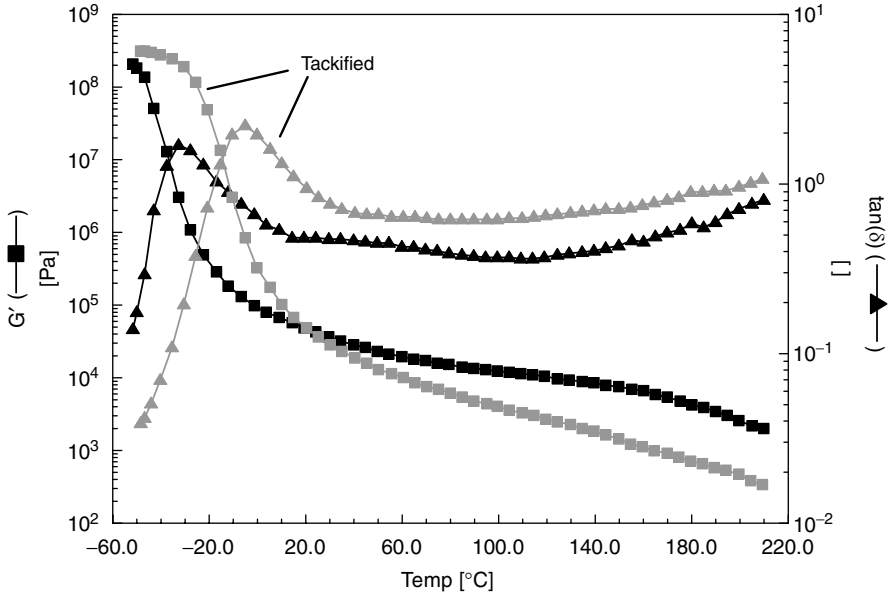


FIGURE 5.23 Effect on G' and tan δ of tackifier addition to an acrylic PSA.

of the tackifiers used with acrylics are unsaturated; thus, resistance to oxidation and discoloration is compromised. This may be acceptable in a temporary label but not in an application requiring long-term durability. One of the principal benefits of acrylic PSAs vis-à-vis rubber–resin formulations is their absence of color and excellent aging resistance. Because the addition of tackifier tends to diminish these advantages, manufacturers often describe such adhesives as "modified acrylics."

5.5.1.2.1 Tackifier Compatibility

Compatibility is the first consideration in selecting a tackifying resin. The choice is limited due to the relatively high solubility parameter of most acrylic PSAs. Rosin acid derivatives, especially esters, are most commonly used, but a number of other classes are useful, including some phenol-modified terpene resins. Nonpolar hydrocarbons and particularly hydrogenated hydrocarbons are unsuitable for use with polar acrylics. Kim and Mizumachi [135, pp. 77–128] conducted extensive studies on the compatibility of tackifiers with a series of solution-polymerized BA/AA copolymers, varying acrylic acid from 0 to 15%. They determined the phase behavior and reported that the blends could be classified into four types: completely miscible over the full range of temperature and polymer/tackifier ratio, completely immiscible, and blends that exhibited either lower (LCST) or upper (UCST) critical solution temperatures. In a few cases, both LCST and UCST behavior was seen. It was noted that the phase diagram often changes from LCST to UCST with increasing acrylic acid content. They also observed that the miscibility tends to decrease with increasing resin molecular weight.

5.5.1.2.2 Tackification with Aqueous Dispersions

Tackification of acrylic emulsions is of considerable commercial importance, particularly for use on paper labels. Tobing and Klein [136] undertook mechanistic studies and explained the loss of cohesion upon tackification as being due to diffusion of the emulsion polymer sol fraction into the tackifier particles. The microgel fraction, once depleted of the linear acrylic polymer chains, was no longer able to form an entangled network. Kim and coworkers [137,138] reported on the miscibility and viscoelastic and adhesive properties of tackified emulsions. During the process of coating and drying, a tackified emulsion a skin may form with the result that drying is retarded. This phenomenon has been studied by Mallégol et al. [139] (see Section 5.6.4).

5.5.1.3 Hybrid (Grafted) Acrylic–Rubber Polymers

Although some improvement in the aging properties of tackified acrylics can be gained by using at least partially hydrogenated rosin derivatives, the formulating options would be greatly increased if synthetic hydrocarbon resins were compatible. To address this need, Mallya and Smith [140] and Foreman et al. [75,141] used a saturated hydrocarbon macromer, poly(ethylene–butylene) methacrylate, to create a grafted acrylic–rubber PSA, with the rubber phase compatible with hydrocarbon resins, including fully saturated resins. The rubber phase is discernible as a second glass transition in the DMA spectrum (see Figure 5.24) [141]. When formulated with a synthetic hydrocarbon resin at 40 pph and cross-linked, the grafted polymer demonstrated considerably greater static shear

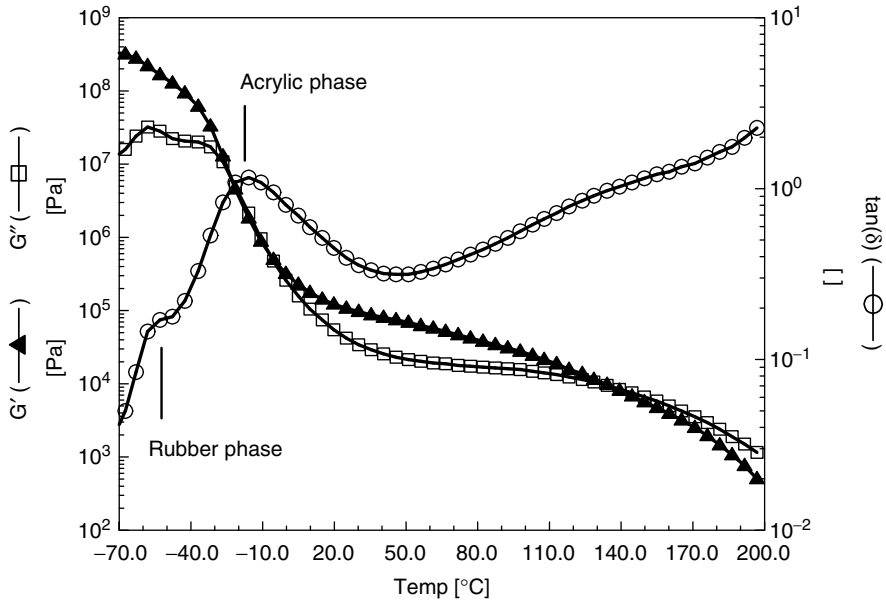


FIGURE 5.24 Rheological properties of a saturated rubber grafted acrylic PSA.

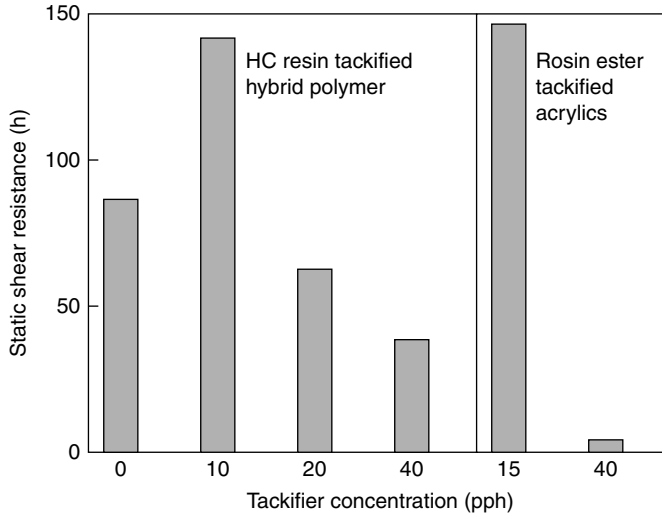


FIGURE 5.25 Effect of tackifier addition on the static shear resistance of hybrid and acrylic polymers.

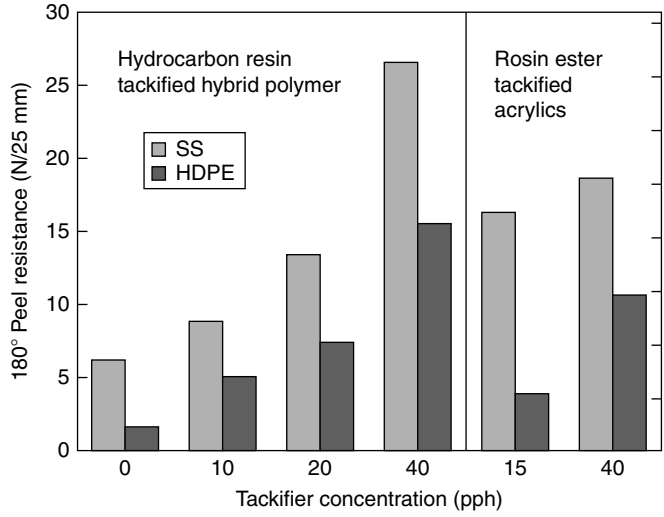


FIGURE 5.26 Effect of tackifier addition on the peel resistance of hybrid and acrylic polymers.

resistance than a cross-linked acrylic formulated with an equal weight of a rosin ester resin with a comparable softening point (Figure 5.25) [141]. This was attributed to the differing polymer architecture, although the result is somewhat surprising in view of the low T_g of the macromer. By comparing the peel resistance (Figure 5.26), it was determined that the tackified grafted polymer exhibited significantly stronger adhesion to both SS

and high-density polyethylene versus the tackified acrylic. The formulated hybrid PSA exhibited very high tack, exceptional adhesion to both PE and SS, reasonable shear strength, and sufficient heat resistance for many tape applications.

5.5.1.4 Compatibilizers for Acrylic and Rubber Polymers

An alternative method of compatibilizing an acrylic PSA with a rubber polymer is to use a suitable diblock polymer, with one block being compatible with the acrylic and the other with the rubber. Nelson et al. [142] prepared diblocks, $M_n \sim 30{,}000$, of 4-vinylpyridine (VP) with either St or isoprene by anionic polymerization. The VP block was compatible with a 90/10 *iso*-octylacrylate/acrylic acid random copolymer and the polyisoprene (PI) and polystyrene blocks were compatible with the mid- and end-blocks of styrene-isoprene-styrene elastomer, respectively. As little as 0.25% PI–PVP diblock added to a 70/30 acrylic–rubber blend significantly reduced the phase separation in solvent cast films and at the 2% level there was a fine microphase separation that remained stable upon high-temperature annealing. When the rubber phase was tackified with a C_5 hydrocarbon resin, the compatibilized adhesive had a large increase in hot shear strength as well as improvement in cold-temperature peel resistance.

5.5.1.5 Plasticizers

The addition of plasticizer increases the polymer free volume and results in a reduction of the plateau modulus and a lowering of the glass transition temperature (see also Chapter 8). Typical plasticizers are 2-ethylhexyl or butyl esters of dicarboxylic acids such as phthalic or adipic acid.

Reduction in T_g is helpful in facilitating low-temperature bonding (see also *Applications of Pressure-Sensitive Products*, Chapter 4). For instance, Peacock et al. [143], in preferred compositions for vehicular graphic marking films, used 4–6% Santicizer® 97, a di(C_7–C_9 alkyl) adipate from Ferro Corporation, Walton Hills, Ohio or the water soluble plasticizer Pycal® 94, a poly(oxyethylene aryl ether) from Uniqema, New Castle, Delaware. This lowered the minimum application temperature to −7°C versus 4°C for an unmodified adhesive. Sufficient shear creep resistance was retained to prevent the film from lifting around raised rivets.

The effect on room temperature adhesive properties is a reduction in the energy dissipated in peeling, that is, a softer peel, as well as a reduction in cohesive strength. This is, therefore, a common method of achieving removable properties (see also Chapter 8). Typically, 2–5% plasticizer might be used for this purpose but higher amounts are possible. For example, Mueller et al. [66] added 10–30% plasticizer to an acrylic emulsion PSA to create an adhesive for peelable labels. A disadvantage of this approach is that the low-molecular-weight plasticizer is free to migrate out of the adhesive layer into the backing, the substrate, or both. Diffusion over time into either layer naturally reduces the level present in the adhesive, thus raising the peel resistance, sometimes to the point where the label is no longer cleanly peelable. Even if it is still removable, the aged label may have become stained by the plasticizer. An additional problem arises with thermal image papers that employ leuco dye technology: unless a barrier layer is included, the image may fade upon contact with the plasticizer (see also Chapter 10). Some polymeric plasticizers have good

compatibility with acrylics and are said to be nonmigratory [e.g., poly(propylene glycol alkylphenyl ether) available as Plastilit® 3060 from BASF, Ludwigshafen, Germany] [2].

The opposite problem of unintended migration of the plasticizer into the adhesive from flexible PVC backings has the effect of reducing peel resistance, sometimes dramatically (see also *Applications of Pressure-Sensitive Products*, Chapter 8). To minimize the change in properties with age, Landin added plasticizer to the adhesive, thus reducing the plasticizer concentration gradient between the backing and the adhesive [144].

5.5.2 Additives to Improve Coating Properties

In a typical product development much thought is given to the adhesive polymer design and perhaps to further compounding to achieve the desired balance of adhesive properties for the intended application. Equally critical, however, to successful commercialization is the ability to produce defect-free coatings at economic production speeds. Coating problems often do not become evident until pilot coating trials are made. (Technological additives are also discussed in Chapter 8.)

5.5.2.1 Thickeners or Rheology Modifiers

When a pressure-sensitive product includes a release liner, the transfer coating method of adhesive application to the liner is generally preferred because it permits subsequent lamination to a wide variety of substrates, which may be unsuitable for direct coating for a number of reasons, including porosity, intolerance of oven drying temperatures, susceptibility to scratches, or the prevention of waste of a costly face stock during adjustment of machine conditions. Low-viscosity emulsions may require a wetting agent or a thickener to prevent dewetting on the release liner. Traditionally, high-molecular-weight water-soluble polymers have been used. These may act primarily by chain entanglements in the aqueous phase or more usually by absorption on adjacent particle surfaces to create a loose, bridged network. Nonionic types such as hydroxyethyl cellulose (HEC) thicken over a wide range of pH, whereas alkali-soluble emulsions require neutralization and can be more difficult to use but, if neutralized with a fugitive base such as ammonia, are less water sensitive in the dried film. HEC is prone to enzymatic degradation, whereas the more highly substituted cellulose ethers are more resistant and thus preferred. With all cellulosic thickeners it is important to prevent oxidative chain scission from residual polymerization initiator, which will cause a reduction in emulsion viscosity during storage.

In currently preferred practice, these traditional water-soluble polymers have often been replaced by associative thickeners, which have hydrophobic groups attached to the ends of a hydrophilic backbone. The hydrophobic chain ends are capable of interacting with a particle surface as well as with nonadsorbed hydrophobic groups. In the serum they segregate into micelle-like aggregates to form reversible three-dimensional network structures. Emulsion PSAs thickened with associative polymers exhibit a reduced tendency to shear thinning during coating, which is a benefit to maintaining wet film continuity. A complication in their use is a strong dependence of the fluid rheology on the surfactants and their concentration. As the surfactant concentration increases, there is an increase in viscosity up to a point beyond which it decreases rapidly. This has been attributed to the formation of mixed associative polymer–surfactant micelles.

As the micelles come into closer proximity with one another, polymer loops associated with a single micelle are converted to intermicellar bridges, thus strengthening the network. However, as the concentration increases and surfactant micelles are formed in increasing numbers, the probability of finding more than one associative polymer hydrophobe per micelle decreases leading to a collapse of the network [145].

The choice of thickener plays a critical role in the production of defect-free coatings. Excessive shear thinning behavior may lead to dewetting, causing fish eyes or retraction at the edges of the coating. In knife and roll coating periodic instabilities may be formed on the coated web. If the aqueous phase network structure recovers too rapidly to permit leveling, these will persist as ribs or cascading defects in the dried film. The fluid dynamics leading to ribbing and windows of stable operation have been reviewed by Coyle [146].

5.5.2.2 Defoamers

The tendency for foam to be formed can be reduced by appropriate choice of emulsifiers and wetting agents. For example, acetylinic diols, when used as wetting agents, orient in foam lamellae to reduce their intermolecular attraction, thereby reducing foam stability. However, a defoamer will normally be necessary to control foam resulting from air entrainment during pumping and high-speed coating operations. Defoamers are insoluble materials and may be liquids or mixtures of liquids with hydrophobic solid particles such as silane-treated inorganic oxides, which need to be uniformly mixed before weighing and addition. Very often the effectiveness decreases with time due to adsorption by the polymer particles or perhaps a gravitational separation from the bulk of the emulsion polymer. It is therefore often necessary to evaluate a number of defoamers to find one that is both effective and persistent in its action. Defoamers are used at low levels, typically about 0.1%, to minimize coating defects such as fish eyes.

5.6 Film Formation

In homogeneous polymer solutions evaporation of the solvent leads to increasing chain entanglement and in the late stages of drying the process becomes diffusion controlled. The process of latex film formation is more complicated and has been widely studied because it is of considerable importance in determining the mechanical properties and the distribution of surfactants within the film. In the simplest model, drying is distinguished by three stages: evaporation of water leading to a close packing of particles, elimination of voids by particle deformation, and finally diffusion of the polymer across particle boundaries to create a continuous film in which individual particles become indistinguishable. In practice, as discussed below, intraparticle cross-linking and serum phase surfactants act to inhibit the final stage from reaching completion. A generalized model describing regimes in which particle compaction is driven by sintering and capillary actions has been developed by Routh and Russel [147].

Conventional surfactants are well known to detract from water resistance in the dried PSA film. Aside from possible minor incorporation via transfer reactions, they are physically adsorbed to the particle surface and in dynamic equilibrium with the aqueous phase. Upon drying, the surfactant may plasticize the polymer, if sufficiently compatible, or desorb, creating a nonuniform distribution within the adhesive film.

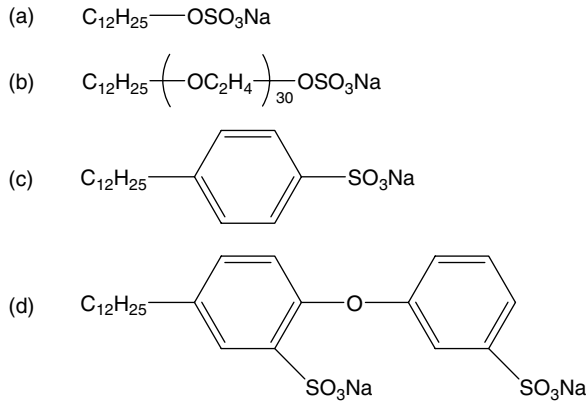


FIGURE 5.27 Surfactants used to study effect on peel resistance: (a) SDS, (b) ethoxylated ether sulfate, (c) SDPS, (d) SDED.

The result may be formation of hydrophilic domains in the form of inverted micelles within the film or a migration to the air interface, depending upon factors such as surfactant composition, molecular weight, and the kinetics of drying.

5.6.1 Effect of Surfactant on Peel Resistance

Zosel and Schuler [148] compared emulsions of poly(ethylhexyl methacrylate) polymerized using four different anionic surfactants (Figure 5.27) to those prepared by postaddition of these same surfactants to a surfactant-free latex. At low peel rates, where cohesive fracture occurred, the peel resistance was independent of the surfactant properties but at higher peel rates, where primarily interfacial failure occurred, large differences were seen. By examining the effect of annealing at 60°C it was determined that an ethoxylated ether sulfate was immobilized on the particle surfaces in the polymerization process, possibly by grafting, but not when postadded. Sodium dodecyl diphenyl ether disulfonate (SDED) was immobilized, irrespective of the method of introduction into the latex. Because grafting cannot explain this, the authors hypothesized that the two ionic groups may give rise to a kind of network structure. Two other surfactants, SDS and sodium dodecyl phenyl sulfonate (SDPS), reduced interfacial strength significantly compared with the surfactant-free latex when polymerized, more so when postadded, and demonstrated a dramatic reduction of interfacial strength upon annealing. This indicated that they were not anchored, but easily capable of migration to surfaces or interfaces. (The influence of surfactant on the adhesive properties is also discussed in Chapter 8, and *Applications of Pressure-Sensitive Products*, Chapter 8.)

5.6.2 Effect of Surfactant on Mechanical Stability and Water Resistance

Amalvy et al. [114], in comparing the polymerizable surfactant sodium tetradecyl 3-sulfopropyl maleate (M14) with anionic surfactant SDS as a polymerization stabilizer,

determined that the surfmer gave improved latex shear stability and reduced film water absorption. An interesting observation was that the *rate* of water uptake was faster in the case of M14. The authors suggested that this might be due to diffusion of water in a percolating structure as opposed to diffusion in a hydrophobic matrix between isolated domains of surfactant. Using ATR-FTIR spectroscopy they demonstrated that surface exudation of surfactant was eliminated by using the surfmer. Aramendia et al. [149] employed atomic force microscopy (AFM) and Rutherford backscattering spectroscopy (RBS) to obtain surfactant depth profiles in BA/MMA/AA latices stabilized with either M14 or SDS. They similarly reported that SDS migrates to the dried film surface and that this increases with annealing temperature, especially above the glass transition temperature of poly(acrylic acid).

5.6.3 Effect of Film Structure on Adhesive Properties

Despite their low glass transition temperature, which assures formation of a continuous film upon drying, the particulate nature of a conventional emulsion PSA remains evident in the dried film when examined by techniques such as AFM of cryogenically ultramicrotomed surfaces. In one of many studies by different groups, Charmeau and coworkers [150] examined the effect of latex structure on stress–strain behavior and peel energy. The results were compared with films cast from an organic solution of the latex. They determined that Young's modulus of the latex films was systematically higher than that of the solution films, which they attributed to polar interactions in a continuous phase of hydrophilic shells surrounding the latex particles. Conversely, the adhesion energy of latex films was always smaller than that of the solution film counterpart. In interpreting this observation they suggested that the solution film, having a continuous soft phase, permits more energy to be dissipated during peeling. Differences in wetting and surfactant distribution at the interfaces were also considered possible contributory factors.

Beyers, Kirsch, and colleagues reported on structured aqueous dispersion particles prepared by a two-stage process in which monomers swell a preformed emulsion seed [151,152]. In the first stage, poly(butyl acrylate) was copolymerized with various carboxylic acids (AA, MAA, and itaconic acid). The seed latices were then swollen with either 6 wt % styrene or 6 wt % MMA and further polymerized. Owing to low polymerization rate constant and high hydrophobicity, the polystyrene domains were found predominantly inside the particles, whereas the PMMA domains were distributed between the surface and the inner part. This is illustrated in Figure 5.28, where dark areas are a pictorial representation of tapping mode (TM) AFM phase images illustrating the distribution of hard, cohesive domains located within the particle and on the particle surface. The morphology of the dried films was compared, using TM-AFM, to mixtures of the component phases prepared as two separate dispersions. The combination of MAA in the seed latex and MMA as the swelling monomer gave the highest shear and peel resistance, exceeding the values obtained with the best unswollen seed latex (which was BA/AA); see Figure 5.28 [151]. They further demonstrated [151] that it was possible to prepare a dried film that resembled a two-dimensional structure of a binary

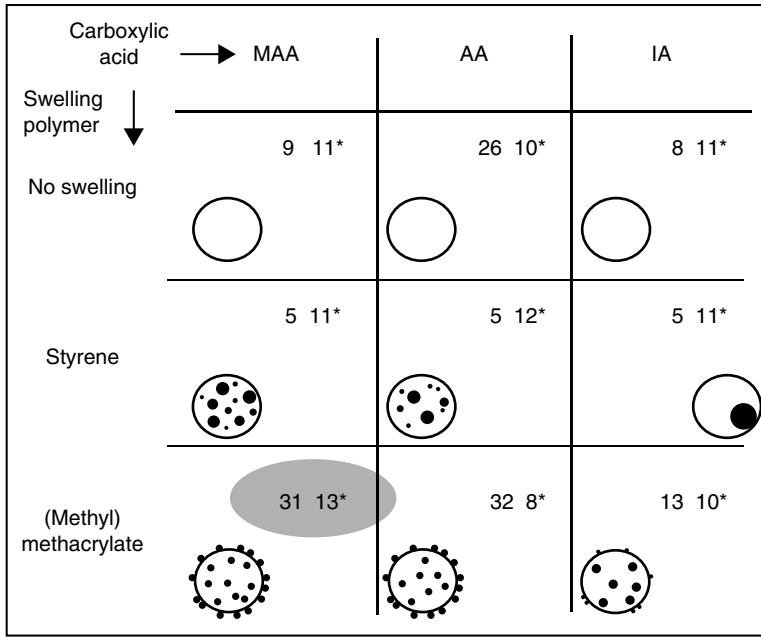


FIGURE 5.28 Shear and peel (*) of dried dispersions with different chemical composition and morphology. (Reprinted from proceedings of *PSTC 30th Annual Technical Conference*, Orlando, FL, 2007. With permission.)

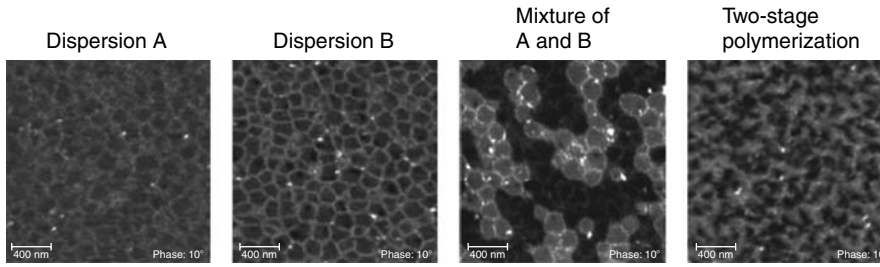


FIGURE 5.29 Cross-sections of dried dispersion films (Dispersion A, Dispersion B, a mixture of A and B, and a two-stage polymer with the composition of A and B) measured by AFM. (Reprinted from proceedings of *PSTC 30th Annual Technical Conference*, Orlando, FL, 2007. With permission.)

polymer solution after spinodal demixing (Figure 5.29) using the two-stage polymerization process. In this film the discrete particles were no longer visible using AFM. This was compared with the hard and soft phase materials mixed as two separate dispersions (Figure 5.30). The film resembling bicontinuous phase morphology, prepared by staged emulsion polymerization, outperformed the polymer blend in both peel resistance and cohesion.

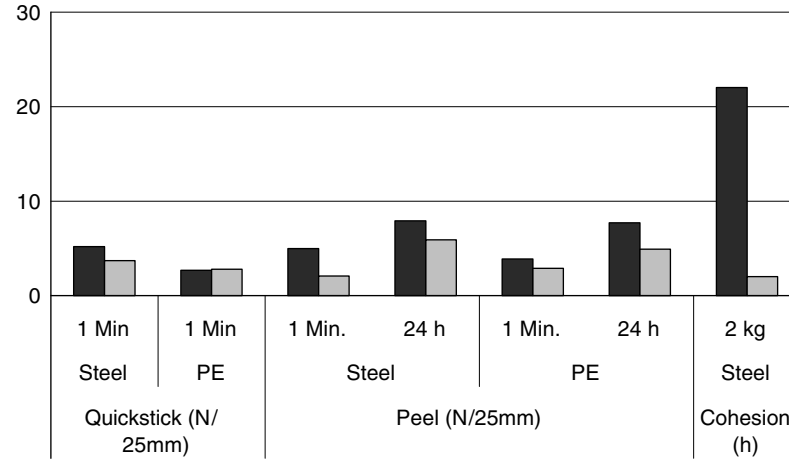


FIGURE 5.30 Comparison of the adhesive properties of a mixture of Dispersion A and Dispersion B (■) and the stage polymer with the composition of A and B (■). (Reprinted from proceedings of *PSTC 30th Annual Technical Conference*, Orlando, FL, 2007. With permission.)

5.6.4 Effect of Tackifier on Film Formation

Skin development during film formation of tackified emulsion PSAs has been studied using AFM in combination with magnetic resonance depth profiling of the film as it dries [139]. The technique, known as GARField (gradient at right angles to the field), measures the proton resonances to obtain the depth profile of water within the film. Researchers reported significant differences in drying mechanism in comparison to an untackified acrylic latex. In the absence of tackifier, in the later stages of drying the water was pinned at the air interface and the concentration increased with depth, enabling surfactants and other water-soluble species to remain distributed throughout the film and inhibit particle coalescence. With 25 wt % and higher levels of tackifiying resin, a skin formed and drying times were significantly retarded. The resin acted to compatibilize the latex particles and serum solids, resulting in particle coalescence. Using RBS, they determined that excess surfactant was present at the air–film interface of the neat latex film, whereas no excess was observed in the tackified film.

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6

Silicone Pressure-Sensitive Adhesives

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6.1 Science and Technology Overview **6**-1
What Are Silicones and Silicone Pressure-Sensitive Adhesives (PSAs)? • Why Silicone Pressure-Sensitive Adhesives and Their Unique Performance Properties? • Delivery Systems for Silicone Pressure-Sensitive Adhesives • Chemistry and Properties of Silicone Pressure-Sensitive Adhesives
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6.1 Science and Technology Overview

6.1.1 What Are Silicones and Silicone Pressure-Sensitive Adhesives (PSAs)?

Silicones are a commercial name for numerous silicone-based products. Technically, silicones (more accurately called polysiloxanes) are polymers with the chemical formula $[R_2SiO]_n$, where R may be an organic group of wide variations including methyl, phenyl, alkenyl, and hydrogen. Structurally, silicones consist of an *inorganic* silicon–oxygen backbone (…–Si–O–Si–O–Si–O–…) with *organic side groups* attached to the silicon atoms, which are four-coordinate. Most often the organic side groups are hydrocarbons such as methyl and phenyl. The inorganic–organic polarity nature gives silicones their uniquely low surface tension. In some cases, organic side groups (e.g., vinyl, hydride) can be used to link two or more of these –Si–O– backbones together. By varying the –Si–O– chain lengths, side groups, and cross-linking, silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from low-viscosity fluids to high-viscosity polymers (gums) to solid resins or from soft

conforming gels to tough elastomers to hard rigid coatings. The most common siloxane is linear polydimethylsiloxane (PDMS), a silicone oil or polymer. The second largest group of silicone materials is based on silicone resins, which are branched and cage-like oligomeric siloxanes.

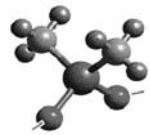
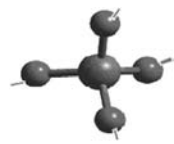
Silicones possess rather unique chemical structures that give rise to unusual intramolecular properties. The Si–O bond on the silicone backbone has a bond energy of 108 kcal/mol, which is significantly higher than the C–C bond of 335.9 KJ/mol and the C–O bond of 339.1 KJ/mol. The commonly recognized bond angle for Si–O–Si is 143°, and O–Si–O is 110°; the bond length for Si–C is 0.188 nm and Si–O has a bond length of 0.163 nm. The siloxane chain flexes and rotates relatively freely around the Si–O axis. These properties of the siloxane backbone give it usually high chain mobility and high chemical stability to degradation. This may also explain why silicones have a very low glass transition temperature, T_g, of around −125°C. Polarity between the Si–O inorganic backbone and dimethyl groups on PDMS and low intermolecular interactions among the methyl groups are responsible for the low surface tension property of PDMS, at 24 mN/m or even slightly lower for lower-molecular-weight PDMS. Silicones are also known to have excellent high-temperature stability (beyond 250°C), display chemical inertness (lack of chemical reactivity) with a number of chemicals, and be environmentally stable [to oxygen, ultraviolet (UV) light, and moisture].

To better describe the chemical structure of various silicones in a simple yet technically accurate manner, an abbreviated symbol system was adopted [1]. The definition and characteristics of the common building blocks for silicones are presented in the Table 6.1.

Pressure-sensitive adhesive (PSA) is a class of precured or preformed adhesive that adheres to a substrate under light pressure. Generally, a PSA has a cohesive strength that is much higher than its adhesion-to-substrate strength. Silicone PSAs are essentially composed of high-molecular-weight silicone polymers and *MQ* siloxane resins (M is trimethylsiloxy or $CH_3SiO_{1/2}$ unit, and Q is silsesquioxane or $SiO_{4/2}$ unit) at a selected ratio and offer numerous unique properties that are inherent of silicones. Many of these superior silicone PSA properties are well connected to the inherent nature of silicones, including their flexibility over a wide temperature range, low intermolecular interactions, low surface tension, thermal stability, UV transparency, high-temperature stability, excellent electrical insulation properties, chemical resistance, and outstanding weathering resistance.

This chapter addresses silicone PSA technology with a special focus on its unique chemistry, properties, processing, and applications. The technological importance of the silicone PSA is best appreciated through its commercial and industrial applications, particularly their persistent and ever-increasing importance in a wide range of industries and applications. Adhesives that contain a small fraction of silicones or silanes as modifiers are outside the scope of this chapter, as are adhesives that deal with silica as a filler or additive. A review on recent advances in silicone PSA technology in public domains was recently conducted by the authors [2].

TABLE 6.1 Common Building Blocks for Silicones

Formula Type	Stereo Model	Symbol	No. Linkage to Oxygen	Wt % [SiO] (Inorganic) (%)
$(CH_3)_3SiO_{1/2}$		*M*	Mono	44.5
$(CH_3)_2SiO$		*D*	Di	59.5
$(CH_3)SiO_{3/2}$		*T*	Tri	77.6
$SiO_{4/2}$		*Q*	Quadri	100.0
$(C_6H_5)_2SiO$		*D′*	Di	22.3
$(CH_3)(H)SiO$		*D′*	Di	73.4

6.1.2 Why Silicone Pressure-Sensitive Adhesives and Their Unique Performance Properties?

Market research demonstrates that silicone PSAs represent only a small fraction of the overall market for PSAs, but they are a very important class of adhesives used in a wide range of different applications [3] (see also *Applications of Pressure-Sensitive Products*, Chapter 4). These applications, however, tend to be highly specialized and "niche" in nature compared with the vast range of applications in which PSAs are used. Silicone PSAs differ significantly from most organic-based (i.e., nonsilicone) PSAs in their basic properties; it is in fact these "special" (and in some cases almost unique) properties that have led them to being preferred over other PSAs in a number of specialized applications.

The key advantages of silicone-based PSAs over conventional organic PSAs are as follows.

- Temperature stability: The key property of silicone PSAs (and silicones in general) is their excellent temperature stability. This is especially important at high

temperatures, but also true at very low temperatures. The typical temperature range over which silicone PSAs are stable and will still behave as PSAs can be from −100 to 260°C, although in some applications they can perform beyond these limits.
- Chemical resistance: Silicone PSAs exhibit excellent chemical stability under acidic or basic conditions; as such, they may be used in "etching" or "chemical cleaning" operations. They also exhibit moderate stability toward different solvents.
- Environmental stability: Silicone PSAs exhibit excellent stability toward moisture, "weathering," and UV, which make them ideally suited to outdoor use where long-term stability is important.
- Flexibility: Silicone PSAs are very flexible, demonstrate good conformability, and can be cleanly removed, which makes them well suited for "masking" applications where a specific surface must be protected. The rheology of Si PSAs is also responsible for their vibration dampening properties.
- Low-surface-energy adhesion: Owing to the fundamentally low surface energy of silicones, Si PSAs demonstrate excellent adhesion to low-surface-energy substrates. They will even adhere to surfaces contaminated with moisture or oil.
- Electrical resistance: Silicone PSAs are essentially nonconductive and therefore can be used in some applications where electrical insulating properties are important (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Other useful properties that make silicones and silicone PSAs suitable for medical applications include the following.

- Low chemical/drug reactivity: "Medical grade" silicone PSAs are further treated to remove silanol groups in the matrix to ensure compatibility (lack of potential reaction) with drug actives (see also *Applications of Pressure-Sensitive Products*, Chapter 4).
- Low toxicity: Silicones and silicone PSAs have been used in many medical devices and applications.
- High gas permeability: Silicones and silicone PSAs have excellent oxygen permeability and high water vapor transmission rate (MVTR). For instance, at 25°C the oxygen permeability of silicone rubber is approximately 400 times that of butyl rubber, making silicone PSAs uniquely useful for medical applications (although precluding it from applications where gas-tight seals are necessary).

The key limitations of silicone PSAs in comparison to organic PSAs are as follows.

- Adhesion: Although the adhesive strength of silicone PSAs is suitable for many applications, they nevertheless have lower adhesive strengths than can be achieved with some organic PSAs. Where high adhesive strength is required, silicone PSAs may not be the most cost-effective solution.
- Low-surface-energy adhesion: The low-surface-energy adhesion of silicone PSAs is an advantage in many applications, but it also implies one large drawback, namely, that Si PSAs cannot be "released" from normal silicone-based release

liners (they adhere too well to silicone release liners). In some self-adhesive constructions (particularly labels), this would pose severe problems (see also *Applications of Pressure-Sensitive Products*, Chapter 4). It is possible to get around this problem using fluorosilicone release coatings, but these special release coatings are costly and tend to be used only for a few specific applications.

6.1.3 Delivery Systems for Silicone Pressure-Sensitive Adhesives

Conventional silicone PSAs are delivered in solvent, specifically in toluene or xylene. This is because silicone PSAs utilize high-molecular-weight silicone polymers (or gums) with a molecular weight (M_w) in the 600,000- to 1,000,000-Da range and *MQ* siloxane resins that are friable solids when solvent-free. Furthermore, commercial silicone PSAs are generally manufactured at 50 to 60% solids in solvent to keep the product viscosity in a manageable range ($<$80,000 mPa · s) at the converters. However, increasing concerns regarding volatile organic compound (VOC) emission and the requirement for solvent/waste handling and processing equipments are the major drawbacks for solvent-based PSAs.

Producers of silicone PSAs have been seeking new chemistry and delivery systems that eliminate or minimize their VOC content. Alternative delivery systems generally fall into one of four categories: liquid solventless and high-solids PSAs, applicable by either traditional converting process or by screen printing techniques, aqueous PSA emulsions, and hot-melt PSAs (HMPSAs).

6.1.3.1 Liquid Solventless and High-Solids Pressure-Sensitive Adhesives

Low-viscosity, functional silicone polymers and *MQ* resins that are curable via thermal or UV radiation cure are the chemical approaches. These systems usually contain curable silicone systems with components containing silicon-bonded hydride (SiH) with silicon-bonded vinyl (Si–Vi) or silicon-bonded epoxy or acrylate functionalities. The main limiting requirement for using this delivery system is the product's upper viscosity and processibility using the existing equipment. The use of reactive fluids as diluents often exists in such systems [4–6].

The use of screen or stencil printing techniques affords a wider compositional and viscosity range but requires investment in screen printing equipment (see also Chapter 10). The benefits realized can go beyond solvent reduction to cost reduction, achieved by eliminating a processing step through direct application of the liquid silicone to a finished good rather than via a prefabricated tape. Modification with thixotropic agents (see also Chapter 8) may also allow better placement control during electronic part fabrication [7,8]. The thixotropic behavior allows for a transition from a relatively low viscosity under high shear conditions when pumping the adhesive to a relatively high viscosity under low shear conditions after screen printing.

6.1.3.2 Aqueous Pressure-Sensitive Adhesive Emulsions

Aqueous PSA emulsions are a commercially important delivery system for organic PSAs but are not widely used for silicone PSAs. The use of surfactants is required for making silicone PSA emulsions, which eventually leads to numerous performance implications

caused by the presence of trapped surfactants in the finished silicone PSA matrix. However, the use of silicone PSAs as a component in otherwise organic aqueous emulsions has been reported [9,10].

6.1.3.3 Hot-Melt Pressure-Sensitive Adhesives (HMPSAs)

HMPSAs are another environmentally attractive option for PSA delivery. Although successfully used for organic PSAs, HMPSAs are not as prevalent with silicone PSAs in industrial applications, but the benefits and technology of hot-melt adhesives in health care applications were well presented by Ulman and Thomas [11] (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

6.1.4 Chemistry and Properties of Silicone Pressure-Sensitive Adhesives

6.1.4.1 Silicone Pressure-Sensitive Adhesives and Basic Building Block Chemistry

Conventional silicone PSAs are essentially a solution of silanol-terminated silicone polymers and silanol-functional siloxane *MQ* resin in an aromatic solvent, most commonly toluene or xylene. The silanol-terminated silicone polymers are usually high-molecular-weight PDMS polymers with the general structure of $M^{OH}D_nM^{OH}$, as illustrated in Figure 6.1. Silicone polymers are relatively low in viscosity, even at high molecular weight, in comparison to their organic polymer counterparts. For instance, PDMS polymer with $MD_{50}M$ structure (i.e., 50 *D* units or M_n = 3,600) has a viscosity of 60 mPa · s; PDMS polymer with $MD_{110}M$ (110 *D* units or M_n = 8,000) chain length has a viscosity of 140 mPa · s, and PDMS polymer with $MD_{400}M$ chain length (400 *D* units or M_n = 30,000) has a viscosity of only 1,440 mPa · s. In contrast, alkanes are only liquid in a narrow range, from C_5H_{12} to approximately $C_{16}H_{34}$. The silicone polymers used in silicone PSAs are generally in the range from high-viscosity fluids to semisolid gums with a molecular weight (M_w) in the 600,000- to 1,000,000-Da range to achieve useful adhesive properties.

Copolymers of dimethylsiloxane $(CH_3)_2SiO$ and diphenylsiloxane $(C_6H_5)_2SiO$, with the general structure $M^{OH}D_mD^R{}_nM^{OH}$, are found in commercial silicone PSAs, where M^{OH} is a

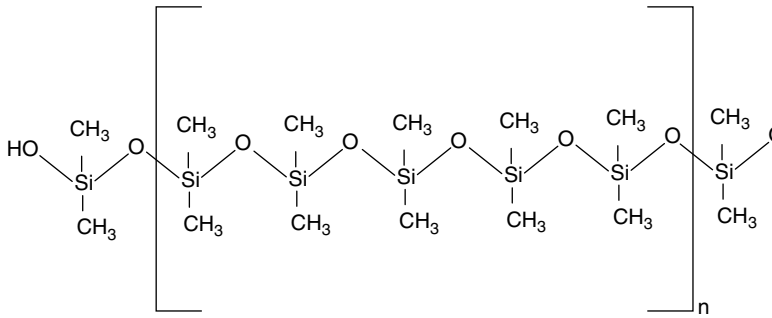


FIGURE 6.1 Schematic of the silicone polymer structure.

hydroxydimethylsiloxy unit, *D* is a dimethylsiloxy unit, and D^R is a diphenylsiloxane unit. It is generally understood that silicones containing diphenylsiloxane units offer improved adhesive properties, particularly at elevated temperatures, and possibly improved organic compatibility. However, the presence of diphenylsiloxane causes a rise in the glass transition temperature, T_g, and stiffening of the silicone polymer backbone; therefore, the amount of diphenylsiloxane in a silicone polymer is quite limited (usually $< 20\%$).

Siloxane resin is the other major component in silicone PSAs. Siloxane resin represents a broad range of siloxane materials. The most common siloxane resins that are useful for making silicone PSAs are *MQ* resins composed primarily of *M* (trimethylsiloxy or $CH_3SiO_{1/2}$) and *Q* (silsesquioxane or $SiO_{4/2}$) units; although many other combinations (*MDT*, *MTQ*, and *DTQ*) can also be used. The siloxane resins that are useful for silicone PSA preparation are silanol-functional siloxane resins (also referred to as silicate in some literature). They are more accurately represented as $[M_xQ]_m$ where *x*, the ratio of *M:Q*, is typically in the range of 0.6 to 1.2:1, and *m* is a variable corresponding to the size (molecular weight) of the *MQ* resin. *MQ* siloxane resins found in silicone PSAs typically have a number-average molecular weight in the range of 1,000–10,000 g/mol.

MQ resins can be synthesized from sodium silicate and chlorosilanes via a rather complex process and delivered in a hydrocarbon solvent, such as toluene or xylene. The *M:Q* ratio and silanol content are carefully controlled during the manufacturing process to yield resins of the desired structure. Characterization of an *MQ* resin structure is a complex task, such that the variants are usually expressed in terms of solution viscosity in toluene or xylene. The neat, solvent-free *MQ* resin is a friable solid with a glass transition temperature in the range of 270 to 350°C, depending on the values of *x* and *m*.

Structurally, *MQ* resin is a highly branched, three-dimensional network, with the extent of branching/networking depending on the exact molecular weight and *M/Q* ratio. A computer-generated molecular model for an *MQ* resin with a three interconnected cage-like structure was recently published by Mitchell [12]. The image in Figure 6.2 illustrates that the *MQ* resin in its fully extended form is a core of three-dimensional *Q* units ($SiO_{4/2}$) surrounded by a shell of *M* units ($Me_3SiO_{1/2}$).

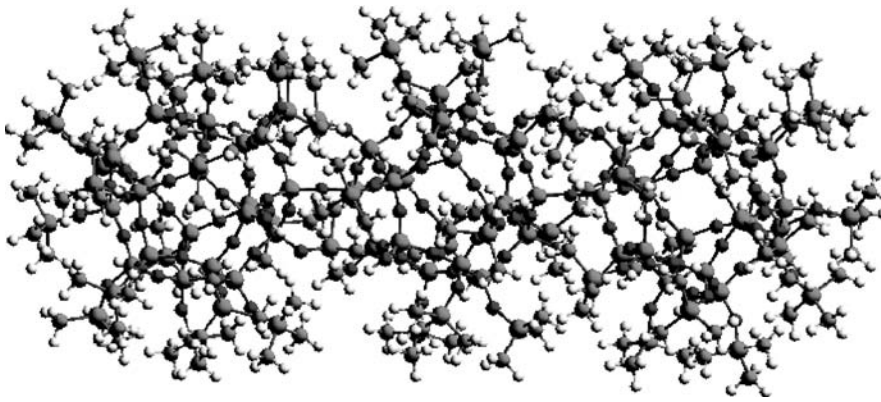


FIGURE 6.2 Computer model of the postulated *MQ* siloxane resin structure.

6.1.4.2 Need for Cross-Linking of Silicone Pressure-Sensitive Adhesives

Neither silicone polymer nor *MQ* siloxane resin exhibits adhesive characteristics. The mixture of silicone polymer and *MQ* siloxane resin in an appropriate ratio exhibited rather fascinating adhesive properties: good peel adhesion and probe tack adhesion; it was later realized that this "cold-blended mixture" lacked cohesive strength and lap shear strength at elevated temperatures. The formation of a network structure between a silicone polymer and *MQ* resin is required to achieve improved cohesive strength and lap shear properties. With this in mind, some degree of covalent bonding process between the silicone polymer and the resin is carried out by the PSA manufacturer, typically by performing a base-catalyzed condensation reaction through the silanol functionalities on the siloxane *MQ* resin and the terminal silanols of the silicone polymer. The reacted product is often referred to as "bodied" silicone PSA. A schematic illustrating such a reaction process is illustrated in Figure 6.3.

6.1.4.2.1 Peroxide-Initiated Free Radical Cross-Linking

Pressure-sensitive tapes coated with as-supplied silicone PSAs exhibit good adhesive properties; however, an additional cross-linking reaction is most often carried out at the tape converters to create further networking of the adhesives to achieve better cohesive strength at high temperatures. The cross-linking of silicone adhesives is either via peroxide-initiated free-radical reaction or via platinum-catalyzed addition reaction, depending on the type of silicone PSA chemistry.

Peroxides, particularly 2,4-dichlorobenzoyl peroxide and dibenzoyl peroxide, are used as the source of free radical to effect cross-slinking in silicone PSAs and are incorporated in the form of solution. Additional solvents and other ingredients such as fillers (see also Chapter 8) and pigments exist in fully formulated PSAs.

The peroxide curing operation is usually carried out in multizoned ovens, with the first zone temperature around 70 to 90°C, so that the solvent can be flashed off from

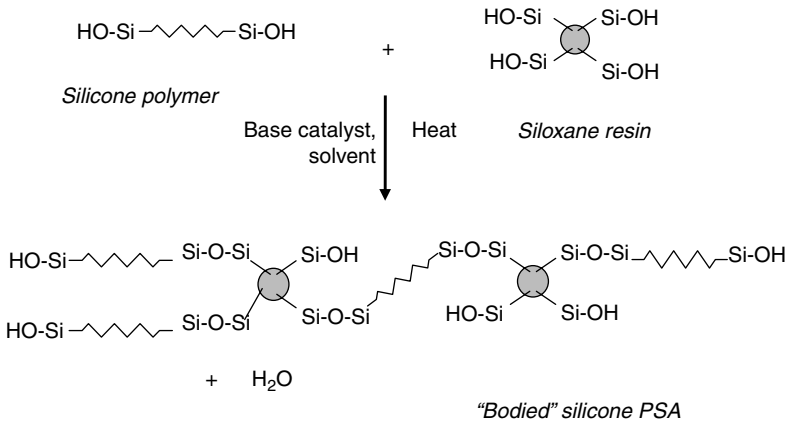


FIGURE 6.3 Preparation of a "bodied" silicone PSA via condensation reaction.

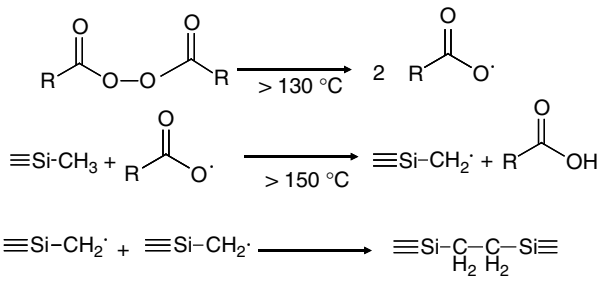


FIGURE 6.4 Peroxide-induced free radical cross-linking of silicones.

the wet adhesive on tape backing well before peroxide decomposition occurs. Peroxide curing of silicone adhesives is a multistep mechanism, as illustrated in Figure 6.4. At elevated temperatures, peroxide is first decomposed into peroxide radicals. The peroxide radicals undergo hydrogen abstraction from the methyl side groups on silicone polymers, which results in the formation of methylene radicals on the silicone backbone. The methylene radicals react with adjacent radicals to form silethylene bridges between the silicone polymers. The peroxide-induced free radical cross-linking reaction occurs most efficiently at high temperatures, typically at temperatures of 130–170°C or higher for 2,4-dichlorobenzoyl peroxide and 150–200°C for benzoyl peroxide catalyst.

Peroxide-initiated free radical cross-linking is a robust cure mechanism that is not susceptible to inhibition. However, the subsequent methylene radical formations and silethylene linkages are nonspecific and nondiscriminating. The peroxide concentration, typically 0.5 to 3% of the silicone adhesive mass, is the main control for the extent of silicone PSA network cross-linking. Peroxide cure results in a more tightly cured adhesive network with better cohesive strength and lap shear strength at elevated temperatures, although some reduction in probe tack adhesion (see also *Applications of Pressure-Sensitive Products*, Chapter 8) is observed at the same time. Some of the disadvantages of this type of silicone PSA system include the handling of volatile solvents and entrapped peroxide by-products within adhesives.

6.1.4.2.2 Addition-Cure Silicone Pressure-Sensitive Adhesives

Addition-cure silicone PSAs offer many process advantages for end users. In recent years, numerous patents have described high-solids and solventless silicone PSAs via the use of addition-cure silicone chemistry, primarily to address the VOC emission issue of solvent-based silicone PSAs [4,6–8,12–14]. In addition, the Pt-catalyzed addition reaction is site specific to the functional groups on the polymers or resins, can occur at relatively low temperatures (even at room temperature), and generates no by-products. Therefore, addition-cure silicone PSAs can be more energy efficient than the peroxide-initiated free radical cure system.

The silicone polymers in addition-cure silicone PSAs contain reactive functional groups, including silicon-bonded alkenyl-functional (Si–Vi) groups and silicon-bonded hydride-functional (SiH) groups. These reactive silicone polymers are cured by a

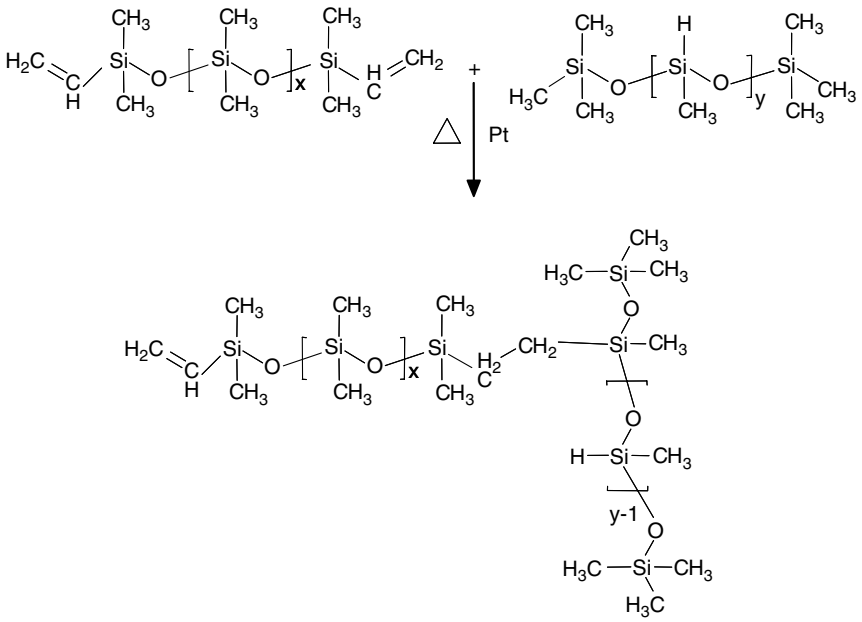


FIGURE 6.5 Formation of a silicone polymer network via silethylene link using a Pt-catalyzed, addition-cure reaction.

platinum-catalyzed reaction of silicon hydride (SiH) to silicon-bonded vinyl (Si–Vi) to form a network via silethylene linkages, as illustrated in Figure 6.5.

A number of parameters are considered in designing addition-cure silicone PSAs, including design of the reactive silicone polymer structure (type and number of alkenyl functional groups per molecule and molecular weight), cross-linker type and structure, type, functionality, and structure of the siloxane resin. The effect of the reactive polymer and cross-linker on addition-cured adhesives has been reported previously [14,15]. The increasing availability of functional silicone polymers has been the enabling key to the development of addition-cure silicone PSAs. Addition-cure silicone PSA composition may further include reactive diluents and additives that target specific requirements for lowering the thermal expansion coefficient, enhancing anchorage, or improving high-temperature properties.

The performance of the solventless and high-solids, addition-cured silicone PSAs are approaching that of the solvent-based silicone PSAs in peel adhesion and probe tack adhesion [3]. An example comparing the peroxide-cure silicone PSAs to the addition-cure silicone PSAs can be found in Table 6.2. However, the lap shear strength at high temperatures still falls somewhat short of that of the solvent-based systems. The literature describes improved compositions that utilize peroxide and addition dual-cure mechanisms or the use of antioxidants to improve high-temperature performance [4,13].

TABLE 6.2 Properties of Peroxide-Cure versus Addition-Cure Silicone PSAs

Type of PSA	Solvent-Based, Peroxide-Cure, Dimethylsilicone PSA	Solvent-Based, Pt-Cure, Dimethylsilicone PSA	Solventless, Pt-Cure, Dimethylsilicone PSA
Peel adhesion[a] (g/2.54 cm)	1,247	1,332	1,049
Probe tack adhesion[a] (g)	1,050	1,280	1,030
Peel adhesion[b] (g/2.54 cm)	737	879	595
Probe tack adhesion[b] (g)	800	1,000	830

[a] PSA on a 50-μm-thick PET carrier.
[b] PSA on a 25-μm-thick polyimide carrier.

Source: Kanar, N. 2006. Silicone PSAs: Trends in the east and west. In: *Proceedings of 29th Pressure Sensitive Tape Council Technical Seminar*, May 2006. With permission.

6.1.4.3 Engineering Silicone Pressure-Sensitive Adhesive Properties

Variables influencing properties and performance of silicone PSAs have been well investigated over the years. Among these variables, the *MQ* resin content and structure are two of the most important parameters to be leveraged. For instance, the peel adhesion of silicone PSAs increases with *MQ* resin content in the silicone PSA, up to a level where maximum peel adhesion is observed. Beyond this maximal resin level, the peel adhesion value begins to drop and eventually the adhesive becomes too nonadhesive to test. The probe tack of silicone PSAs follows a similar trend, except the probe tack reaches the maximum value at a different *MQ* resin content and the drop-off rate is faster than the peel resistance curve. The *MQ* resin content in commercial silicone PSAs is typically in the 50 to 65% bw range to yield optimal peel resistance and probe tack. On the other hand, the lap shear strength of silicone PSA increases monotonically with the *MQ* resin content. The composition–property relationships of silicone PSAs are further illustrated graphically in Figure 6.6.

It is well recognized by the designers of silicone PSAs that other variables such as *MQ* resin structure (in terms of molecular weight and functionality) and silicone polymer structure can significantly influence these adhesive properties.

To further understand how silicone polymer types influence the composition–property relations within silicone PSAs, Lin and colleagues [16,17] compared three silicone PSAs derived from dimethyl silicone and two diphenylsiloxane-containing silicone polymers. "Methyl SiPSA" is a dimethyl silicone polymer with a general structure of $M^{OH}D_mM^{OH}$. "Low phenyl SiPSA1," with a general structure of $M^{OH}D_mD^{\Phi}{}_nM^{OH}$, is a silicone copolymer consisting of mostly dimethylsiloxy units and a low level of Φ diphenylsiloxane units. "High phenyl SiPSA2," with a general structure of $M^{OH}D_mD^{\Phi}{}_nM^{OH}$, is a silicone copolymer containing a moderate level of Φ diphenylsiloxane units. The effect on the probe tack of these silicone PSAs is illustrated in Figure 6.7. Significantly higher probe tack is obtained in the "high phenyl SiPSA2," but, as noted previously,

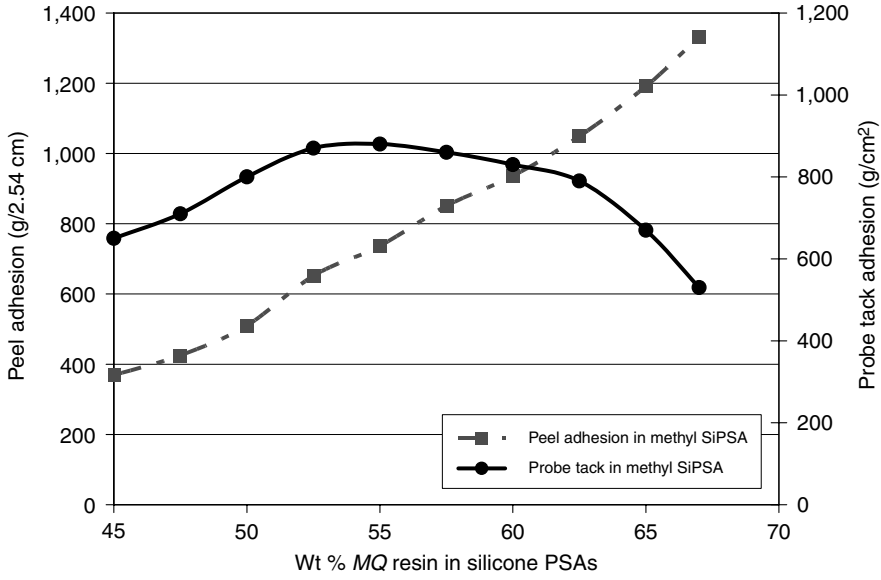


FIGURE 6.6 Influence of the *MQ* resin content on adhesion properties of silicone PSAs.

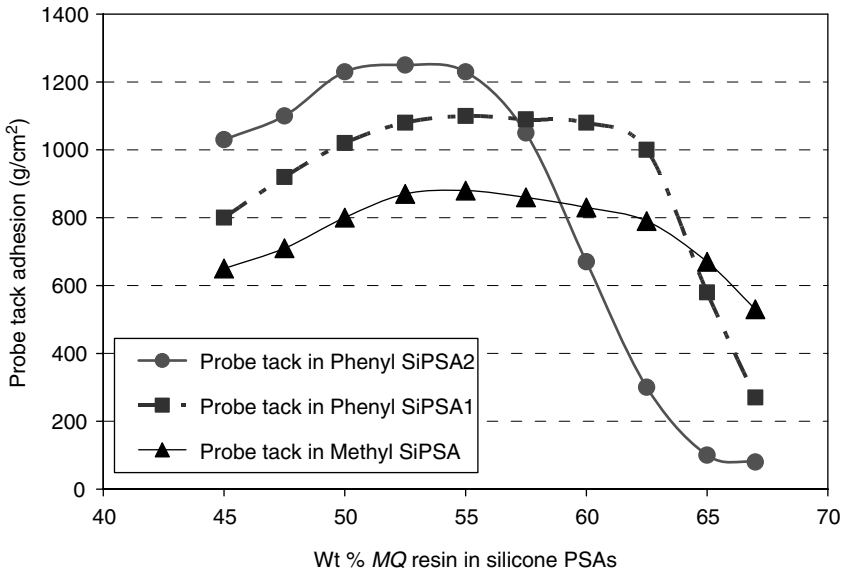


FIGURE 6.7 Effect of silicone polymer type and *MQ* resin content on probe tack adhesion of silicone PSAs.

the adhesive looses its adhesion more quickly with increasing *MQ* resin content. On the other hand, the probe tack is sustained over a broader range of *MQ* resin content in both the "low phenyl SiPSA1" and the "methyl SiPSA."

Rheologic studies were carried out to better understand the composition–property relationships of these silicone PSAs [16]. The elastic modulus G' and the glass transition temperature T_g of silicone PSAs of specific compositions and those of the corresponding gums, and *MQ* resins were determined. These studies indicated that a two-phase structure exists in silicone PSAs—a "resin-rich" phase and a "gum-rich" phase—and demonstrated the importance of polymer–resin interaction and the mutual solubility in silicone PSA rheology [16,17]. Shown in Figure 6.8 is the proposed multiphase structure model for silicone PSAs. The specific phase compositions in the three silicone PSAs were derived from the rheologic data, aided by the Flory–Fox equation. The study also provided a direct correlation among the rheologic properties of the silicone polymer, the *MQ* resin, and the PSAs derived from them.

6.1.4.4 Adhesive Preparation, Characterization, and Processing

6.1.4.4.1 Adhesive Preparation

Commercial silicone PSAs are typically supplied at 50 to 60% solids in toluene or xylene with a viscosity in the range of 20,000–80,000 mPa · s. They are rarely used as is by converters and are generally further formulated with peroxide catalyst and additional solvents to a viscosity suitable for the coating equipment. Other additives including pigments and fillers may also be found in fully formulated adhesives, depending on the applications and purposes.

To adequately characterize the adhesive properties in the laboratory, the silicone adhesive materials of interest, as supplied or formulated, are coated to a specific thickness on a reference tape carrier material. Silicone PSAs are coated using a variety of manual or automated draw-down applicators to yield a dry film thickness of 38–50 μm (i.e., 10^{-6} m). The most common film carrier materials for silicone PSAs are poly(ethylene terephthalate) (PET) polyester and polyimide. Other important high-temperature-resistant carrier materials for silicone PSAs include poly(tetrafluoroethylene) (PTFE) film and PTFE-coated Fiberglass cloth.

The coated adhesives on film are cured to yield a PSA tape for testing. The peroxide-catalyzed adhesive is devolatilized at 70–90°C, followed by curing at >160°C for 2 min. The solvent-based, addition-cure adhesives follow a similar two-step schedule to flash off the solvent first, followed by curing at a temperature of around 150°C for 2–3 min. In the case of solventless, addition-cure systems, the cure may be accomplished at a single temperature (e.g., 150°C for 3 min), without the need for a solvent flash step. The exact cure schedule (time and temperature) for all adhesive systems depends on many factors, including film substrate type, catalyst level, and oven efficiency; the practitioners must determine the preferred cure conditions to achieve the best performance.

6.1.4.4.2 Adhesive Characterization

Most of these adhesion tests for PSAs and the values obtained are not just a measure of intrinsic adhesive performance, but are also a function of how the adhesives are prepared and how the tests are conducted. Numerous variables are involved that can affect the test

outcome, including adhesive thickness, tape carrier type and thickness, test panel type, and surface condition. To create consistency within the industry, the common, standardized methods for adhesive testing are well documented in industry association [Pressure-Sensitive Tape Council (PSTC) and Association of European Tape Manufacturers] publications (see also *Applications of Pressure-Sensitive Products*, Chapter 8). These publications contain a wealth of information, informational diagrams, and pictures. They also include cross-references to European Committee for Standardization, International Organization for Standardization, and American Society for Testing and Materials (ASTM) methodologies.

The standard test methods for characterizing silicone PSA performance include peel resistance (ASTM D-3330 or PSTC-101), probe tack (ASTM D-2979), loop tack (PSTC-16), and static lap shear at elevated temperatures (ASTM D-3654 or PSTC-107). The PSTC publication includes test methods that cover various approaches to measuring tack, quick stick, peel resistance, static lap shear strength, release force from substrate, unwind force, and accelerated aging of samples.

One technique demonstrating an increasing importance in PSA characterization is tack measurement using a Texture Analyzer™ from Texture Technologies (Scarsdale, New York). The benefit that the Texture Analyzer has over the historical probe tack tester, which is essentially testing for the same property, is that it gives a graphical representation of the material's behavior by collecting numerous data points during the test cycle. The graphical data provide further quantifiable details for the force and mechanism of bonding and debonding processes. This provides useful insights to the influence of viscoelastic properties on tack. Newer probe tack testers may also incorporate a computer interface for multipoint data collection.

The high-temperature shear adhesion of a silicone PSA is the adhesion strength of the cured adhesive to a stainless steel (SS) plate against a counterweight hung from the laminate at elevated temperatures (see also *Applications of Pressure-Sensitive Products*, Chapter 8). The results of this test are usually recorded as pass/fail relative to a dropped weight at a specified temperature/weight/time condition or distance of tape slippage at a specified temperature/weight/time condition. The test is usually carried out in an air-circulating high-temperature oven and can be an effective test for the thermo- and oxidative stability of the adhesive. It is important to note that the surface condition of the SS test panels can significantly affect the test outcome. In some cases, the smooth SS plate is roughened with fine sandpaper prior to use, whereas in other cases (e.g., testing for residue transfer onto substrates) the SS plate is simply solvent cleaned and dried prior to use.

However, this simple high-temperature lap shear test is not sufficient for applications with minimal outgassing or residue requirements. Visual assessments are made on the adhesives adhering to the SS plate for the propensity for gas bubbles in adhesives, residue formation upon peeling, and ghost pattern formation on the tested SS plate after peel at stepwise temperatures up to >300°C.

The adhesive properties of a PSA depend not only on its surface properties (e.g., interfacial wetting and interaction with adherent substrate), but also on its bulk viscoelastic properties (see also *Fundamentals of Pressure Sensitivity*, Chapters 2, 5, and 6). The rheologic behaviors of PSA materials have been extensively studied for years, and the principal viscoelastic properties that predict the PSA performance have been well established by Carl A. Dahlquist, who was best known for his work to determine the modulus value

of a material necessary for it to be deformable and tacky enough to be considered a PSA. This work is widely known as the Dahlquist criterion.

6.1.4.4.3 Processing and Converting of Silicone Pressure-Sensitive Adhesives

Substrate Preparation Because one of the key features of silicone PSAs is their superior high-temperature performance, they tend to be coated onto substrates that are also capable of withstanding high temperatures. As mentioned previously, the most common substrates are polyimide for high-temperature applications and PET for less temperature-demanding uses. Other substrates used include glass cloths, metal foils, silicone elastomers (unsupported or coated onto textiles), polyamide, PTFE, and PTFE-coated glass cloth.

Whereas silicone PSAs are capable of "wetting-out" onto these difficult-to-adhere-to substrates, a treatment or primer coat is typically applied to enhance the adhesion of the Si PSA to these substrates. Surface treatments, either chemically or by electrical or flame plasma (see also Chapter 10), are applied to generate a modified surface to allow silicone adhesives to bind tightly to the substrate. Chemical etching to "roughen" the substrate surface is a common approach for PTFE and PTFE-coated glass cloths; corona discharge treatment is another common approach for PET. Often, a primer coat is applied to these substrates prior to coating with silicone PSA. The most common primers of industrial importance are essentially variations of dimethyl silicone in solvent systems. Kerr [18] described a phenyl-based primer offering the specific property required to bridge phenylsiloxane-based silicone PSAs and backing materials. Kuroda et al. [19] described a platinum-catalyzed, addition-cure silicone primer composition to effectively improve adhesion between plastic film substrates and silicone PSAs. The chemistry, thickness, and cure extent of the primer coating are important factors to consider for good substrate adhesion.

Coating and Curing of Silicone Pressure-Sensitive Adhesives Silicone PSAs may be applied using a range of different coating techniques, although there are limitations due to the viscosity range of the materials. With a typical viscosity range for conventional solvent-based silicone PSA between 20,000 and 80,000 mPa · s, knife-over-roll, two-roll, slot-die coaters and their variations are the most common coating techniques used to deliver the desired adhesive coat weight over film substrates (see also Chapter 10). Other coating techniques, such as gravure roll and curtain coating techniques, can be used for lower-viscosity adhesive formulations or to deliver a thinner adhesive layer. To a lesser extent, screen printing is also in use, particularly for solventless silicone PSA systems or adhesives with higher viscosity.

The curing of solvent-based silicone PSAs requires first the removal of volatiles from the coated adhesive, followed by peroxide-catalyzed cross-linking of adhesives and is therefore accomplished in a multizone industrial oven with temperature gradients from low to high temperatures. It is essential that solvent volatiles be fully and efficiently removed from the adhesive mass during the flash drying zone, typically at 70 to 100°C, of a multizone oven and prior to the curing zones, with temperatures ramping up to 250°C. Drying that is too fast can cause skinning (a phenomenon where the upper

surface layers of adhesive have been dried, forming a "crust," which then hinders further solvent evaporation from the layers lower down within the adhesive), and drying that is too slow can cause "bubble" formation within the adhesive due to some of the evaporating solvent being trapped within the adhesive layer. Both are problematic and may impact the performance of the final adhesive tapes. In some cases, the solvent can also be subject to the peroxide cross-linking reaction, thus compromising the desired final adhesive composition. The choice of temperature and speed of cure for a peroxide-catalyzed system will depend on many factors (including adhesive thickness, amount of volatiles to be removed, and type of peroxide being used), as well as the oven design, efficiency, and residence times within the oven. The choice is certainly more complex for solvent-based, peroxide-catalyzed adhesive systems.

For platinum-catalyzed silicone PSAs, on the other hand, the "curing" process is much more straightforward. When solvent is present, there is an initial drying requirement to remove volatiles from the platinum-catalyzed silicone PSA so that they are properly dried and cross-linked. The cure chemistry of these adhesives involves cross-linking specifically between the silicon-bonded hydrogen (SiH) on the cross-linker and silicon-bonded alkenyl ($SiCH{=}CH_2$) groups on the base polymer, thus providing little opportunity for the solvent to be involved in the cross-linking reaction (see Section 6.1.4.2.2). Solvent drying and adhesive curing may occur simultaneously. Therefore, the choice of cure temperature and speed will depend mainly on the thickness of the adhesive layer (so as to remove solvent volatiles), and the cure temperature used can be considerably lower than that typically needed for peroxide-catalyzed silicone PSAs. As an example, a typical curing condition for a 50-μm (dry) adhesive layer would consist of 3 min at 100 to 150°C web temperature.

For solventless, platinum-catalyzed silicone PSAs, the curing process is even simpler because there is no requirement for solvent removal stage and all the issues associated with it. The choice of temperature and speed of cure will depend mainly on the thickness of the adhesive layer (so as to reach a desired cure temperature) and, again, the oven temperatures can be considerably lower than that typically needed for peroxide-catalyzed silicone PSAs.

Handling of Solvent Waste and Volatiles A significant amount of solvent is present in as-supplied silicone PSAs and the derived adhesive formulations (typically more than 50% by weight), which emit solvents during the converting operation. There are also issues associated with the silicone volatiles emitted from silicone PSAs; at relatively low concentrations this still adds significant handling concerns to converters.

In some cases, emitted solvents are captured by the use of solvent-capturing equipment; however, the captured solvents are rarely reused for formulations due to contamination with low levels of silicone volatiles (see also Chapter 8). The emitted solvents are mostly disposed of by incineration at most converters. However, low-molecular-weight silicone volatiles, although at a low level, are emitted through a solvent incinerator. These silicone volatiles degrade into silica dust in thermal oxidizers and cause reduction in the efficiency of the solvent incinerators and downtime in adhesive-converting operations. Regular maintenance and cleaning of curing ovens are required to prevent build-up of silica dust.

6.2 Applications for Silicone Pressure-Sensitive Adhesives

6.2.1 Industrial Applications

Organic PSAs exist in many consumer and industrial applications. Silicone PSAs, on the other hand, are used in selected and demanding applications where organic PSAs do not meet the performance requirements. The industrial applications of silicone PSAs can be broadly grouped into three main families in terms of intended use: masking tapes, splicing and process tapes, and high-performance insulation laminates.

6.2.1.1 Silicone Pressure-Sensitive Adhesive Tapes and Release Liners

Silicone PSA tapes are self-wound tapes; that is, the tape is wound up so that the silicone PSA-coated side comes into contact with the uncoated side of the tape substrate (see also *Applications of Pressure-Sensitive Products,* Chapter 4). In some cases, the silicone PSA tape is supplied as a laminate, in which case a release liner is used. Traditional release liners based on standard silicone release coatings will not work against silicone PSAs (the release force will be too high!). It is therefore necessary to use special forms of release liner. This can either be in the form of a "crimped" liner (see also Chapter 10), where the area of contact of liner with silicone PSA is very limited and hence the release force is acceptably low, or it can be in the form of a fluorosilicone release coating, which offers a genuinely low release force against a silicone PSA.

6.2.1.1.1 Masking Tapes

Silicone PSAs are used in masking tapes (see also *Applications of Pressure-Sensitive Products*, Chapter 4) for applications in which the masking tape must withstand multiple cycles of operations under either high temperatures or harsh chemical exposure. Silicone PSAs are uniquely qualified as masking adhesive tape due to their excellent conformability, high temperature stability, and chemical stability. The range of masking applications includes plasma spray tape and wave solder tape.

Plasma Spray Tape Plasma spray tapes are protective masking tapes used during the treatment of surfaces with plasma spraying/flame spraying of many different coatings to protect specific areas from being treated. Masking tapes (and the PSAs) must withstand extreme temperatures used during plasma spraying, where temperatures may exceed 1,000°C in some cases (although exposure time to such temperatures is short). The tapes must also be capable of withstanding the abrasive conditions in some plasma processes (such as "grit blast").

Wave Solder Tape Wave solder tapes are protective masking tapes used during the manufacture of printed circuit boards for electronic applications where parts of the board must be protected against molten solder. The masking tape and PSA must withstand temperatures up to 260°C and be removed cleanly afterward. Recent moves toward lead-free solders mean that even higher temperature stability is now needed (280°C). Only silicone PSAs are capable of meeting such process requirements.

Plating Tape Plating tapes include a range of masking tape applications used to protect specific areas of printed circuit boards during their manufacture from the chemicals used to strip and plate them. For some high-end applications the masking tape must withstand prolonged contact with the chemicals, whereas for other applications it may only be a case of withstanding "splashes" and "fumes" from the caustic chemicals used. The excellent chemical stability of silicone PSAs plus their conformability make them well suited for these applications.

Powder-Coating and Chemical-Processing Tape Such masking tapes are employed in industrial powder coating operations where the tape must withstand the high temperatures (200–300°C) employed in these operations. Silicone PSA-based tapes are also used as masking tapes to protect parts of an aircraft from the aggressive chemicals used during chemical stripping processes, such as the stripping of old paint or the cleaning of aircraft prior to repainting. The high temperature and chemical stability of silicone PSAs plus their conformability make them ideal in this application.

6.2.1.1.2 Splicing and Process Tapes

Silicone PSAs are used as splicing tapes in a number of different applications where substrates, processing conditions, and performance requirements may differ widely, yet silicone PSAs offer the best match to these requirements (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Release Liner Splicing Tape Silicone PSA tapes have long been used as splicing tapes for silicone release liners in their manufacturing operations and uses. The intrinsically low surface energy of silicone PSAs, coupled with their affinity toward silicones, makes silicone PSA ideal in this application. Silicone PSAs are virtually the only kind of PSAs that will adhere well to silicone surfaces. As line speeds in silicone liner production continue to increase, there has been an equivalent shortening in the splicing time, thus requiring ever better performance from the silicone PSA splicing tapes.

Silicone Rubber Splicing Tape Silicone PSA tapes are also used in splicing applications where silicone rubber surfaces (or silicone-coated textile surfaces) must be spliced together and remain together for an extended period of time. An example of this is silicone rubber conveyor belts used in the food industry.

Photographic Film Splicing Silicone PSA tapes are used as splicing tapes for photographic film where rolls of exposed films are processed through automated photographic development machines. The PSA of the splicing tapes must withstand the chemical assault of the development solutions while maintaining a good degree of adhesion to the film. Clean removal of the tape after processing is also important. The chemical resistance of silicone PSAs makes them well suited to this application.

Roller Wrapping Tapes Silicone PSA-coated PTFE tapes (or PFTE/glass cloth tapes) are often used to protect heated rollers in plastic film processing (to give them a nonstick surface), as well as to protect the heating elements in heat-sealing applications to make them nonstick. The PSA must withstand multiple cycles in temperature from room temperature up to as high as 260°C and be easily removed afterward, without leaving

residue behind. The heat stability of silicone PSAs, as well as their adhesion to low-surface-energy substrates such as PTFE, makes them well suited to this application.

Heated Fabrication Tapes Silicone PSA-coated glass cloth/PTFE tapes are used as "sleeves" to protect the heated platens in equipment used to manufacture polyvinyl chloride (PVC) window frames. The sleeves are designed to prevent the hot PVC from sticking to the heated platens, where the PSA may have to withstand temperatures up to 260°C. The high temperature performance of silicone PSAs makes them ideal for this application.

6.2.1.1.3 High-Performance Insulation Tapes

The final group of applications for silicone PSAs includes applications where the electrical insulating properties of silicone are important (coupled with their temperature performance).

Mica Binding Mica tapes are used widely in the manufacture of electrical motors to protect and insulate against heat and electricity, as well as to protect heating elements in household and industrial appliances. These mica minerals typically require a "binder" resin to yield a tape that can be readily processed. For particularly high-temperature applications (in excess of 180°C), silicone PSAs are used as binder resins. The heat stability of silicone PSAs, coupled with their electrical insulation properties, makes them ideal for these applications.

Electrical Insulation Tapes Silicone PSAs are used in electrical insulation tapes for electric cables where the temperature performance requirement is stringent (see also *Applications of Pressure-Sensitive Products*, Chapter 4). The requirement here is not only for high-temperature performance, but also very-low-temperature performance (temperatures as low as −200°C and as high as 260°C). Silicone PSAs are almost unique in their ability to meet this wide temperature range requirement. Silicone PSAs are also used as electrical insulation tapes (typically based on glass cloth as substrate) in applications such as tapes for insulation of armatures and phase insulation in generators and transformers.

6.2.1.2 Medical Applications

Ulman and Thomas have written a good review on the use of silicone PSAs in health care applications [11]. Silicones offer a range of materials and properties to help meet general requirements for medical applications, such as biocompatibility (e.g., biologically inert, nontoxic, nonirritating, and nonsensitizing), efficacy (e.g., suitability for use on skin and permeability to therapeutic substances), and stability (e.g., good chemical inertness and retention of physicochemical properties at skin temperatures), along with a wide range of formulation possibilities to meet specific application needs (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Silicone PSAs are increasingly used in medical applications where the PSA is intended to be in contact with human skin. Silicone PSAs offer such unique benefits as inherently good compatibility with skin, skin adhesion over time, and high moisture vapor and

oxygen transmission rates. Advances in medical silicone PSAs have allowed them to be successfully used for scar therapy devices and in some wound care applications—especially where nontraumatic dressing removal was needed [20].

The low surface energy inherent to all silicone PSAs allows them to have suitable tack and adhesion for a variety of skin types, as well as the ability to wet onto and conform to the skin relief. The medical PSA must provide secure adhesion for the prescribed duration and then have the ability to be removed cleanly from skin without causing undue trauma to the wearer. Resistance to moisture, UV radiation, oxidative effects, and biological attacks are other factors leading to their acceptance in medical applications.

Maceration of the skin can occur when it is consistently wet and is most noticeable by softening and discoloration of the skin to a pale or whitish color. Macerated skin can more easily become infected with bacteria or fungi. Therefore, the likelihood of maceration is reduced if the skin-contact adhesive allows moisture vapors from the skin to escape. To avoid maceration of the skin, most medical PSAs must be permeable to gases and water vapor. The MVTR is a measure to quantify the amount of moisture an adhesive or film will transmit over a given time. Higher MVTR indicates more vapor is allowed through the film or adhesive being studied. Although silicones are very hydrophobic, medical silicone adhesives have MVTR values comparable to that of other solvated adhesives and have found utility in many medical applications, including wound management, diagnostic devices, and ostomy appliances [11].

Silicone PSAs have been used for some time in transdermal drug delivery therapies and their use in these applications continues today. Many pending and assigned patents highlight the ability of silicone PSAs to positively affect the release rates of pharmaceutical actives. Adhesives designed for transdermal drug delivery must demonstrate permeability to therapeutic ingredients, a lack of reactivity in the presence of the active, and the ability to maintain adhesive and cohesive properties in the presence of drugs. Silicone PSAs offer excellent solubility and permeability to lipophilic drugs, but in some cases it is desirable to deliver hydrophilic drugs. The adhesive chemistry can be further modified by formulation with hydrophilic fillers, copolymers, or plasticizers or by modification of the network with silicone–organic copolymers.

Although regulations today do not specify quality and safety operations for pharmaceutical excipients, guidance documents from several organizations (including the International Pharmaceutical Excipients Council, Pharmaceutical Quality Group, and World Health Organization) identify critical good manufacturing principles to consider. Many silicone PSAs are classified as pharmaceutical excipients due their status in transdermal drug delivery patches, and some suppliers of silicone medical PSAs have created drug master files that describe in great detail the chemistry, manufacturing processes, batch history, and toxicology of the adhesive, which can facilitate the approval of the final transdermal device.

PSAs that are designed and used in medical applications ultimately must have the appropriate biocompatibility proven for their specific uses prior to their being selected. Many polydimethylsiloxane derivatives, including some silicone PSAs, are listed with the U.S. Food and Drug Administration as pharmacopoeial excipients providing evidence of the biocompatibility of silicone PSA. PDMS silicones, a key component in silicone PSAs, are used widely in skin lotions and lip balms, lending further confidence

to the acceptability of the silicone PSA's biocompatibility. Silicone PSAs hold a unique biocompatibility profile due to their hydrophobicity and low surface activity. These inherent characteristics deter bacterial growth, limit the interactions with bodily fluids, and provide good chemical stability relative to many other adhesive types. Meeting the requirements of primary skin irritation, sensitization, and cytotoxicity tests are baseline requirements for most skin-contacting applications. The ultimate use and location of the adhesive and the duration of contact may dictate that other studies, including systemic toxicity, subchronic toxicity, genotoxicity, or implantation studies, are also warranted.

There are two variations of silicone PSAs in medical applications: "standard" medical silicone PSA and "amine-compatible" silicone PSA. The standard silicone PSA is a condensed (i.e., "bodied") PDMS silicone with *MQ* siloxane resin dispersion in a volatile solvent. The preparation of bodied silicone PSA via condensation reaction has been previously described (and is illustrated in Figure 6.3). This class of adhesives has gained wide acceptance in transdermal drug delivery devices. Other medical applications for this class of adhesives include wound management devices, ostomy appliances, and diagnostic devices. Other nonmedical skin-contact applications include the attachment of character masks for actors and the application of toupees and wigs to hair-care clients [11].

Standard silicone medical PSA contains a relatively high amount of silanol functionality following the initial condensation. This silanol will readily react with the amine functionalities in many drugs, thereby limiting their use for many transdermal drug delivery systems. To prevent the interactions between the adhesive and drug, the standard adhesive can be further treated with a silane capping agent to yield an endcapped amine-compatible PSA that has relatively inert terminal trimethylsilyl functionality. An illustration of the standard medical silicone PSA and the amine-compatible silicone PSA is illustrated in Figure 6.9.

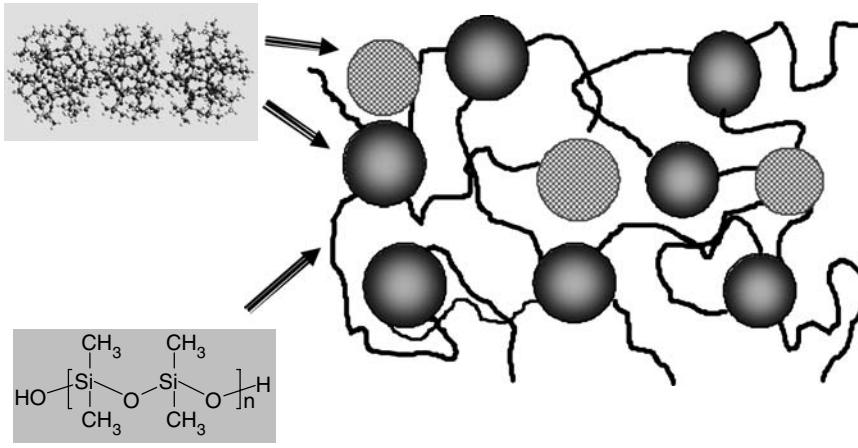


FIGURE 6.8 Proposed multiphase structure model for silicone PSAs.

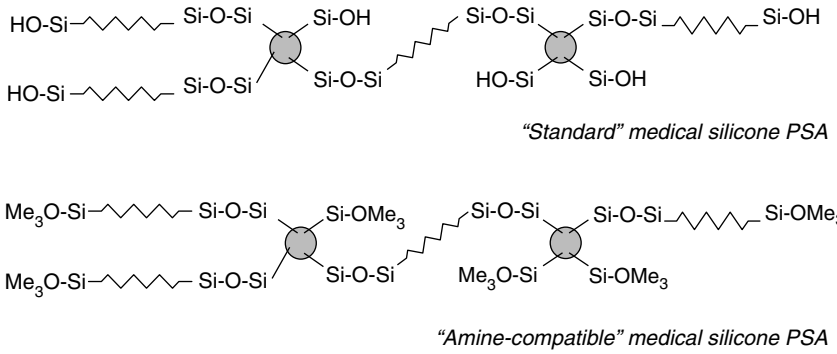


FIGURE 6.9 Depiction of "standard" and "amine-compatible" medical silicone PSAs.

As discussed in the previous section, final silicone PSA properties can be adjusted by varying the polymer-to-resin ratio and the degree of cross-linking of the PSA. During formulation, some resin is required to provide cohesive characteristics of the PSA, and some polymer is required to provide tack and the ability to wet out onto skin. The ability to modify the PSA formulation, process parameters, and end-group functionality to achieve improved chemical stability and precise tack and adhesive properties allows application-specific fine-tuning of the PSA. This formulation flexibility becomes especially important in the field of transdermal drug delivery, which requires formulation with additives in addition to cosolvents, excipients, or skin-penetration enhancers to adjust the cold-flow characteristics of the adhesive. Raising resistance to cold flow can be achieved through the use of cohesive strengthening agents. Optimal loadings are typically in the 10 to 20% range and include such molecules as calcium stearate, magnesium stearate, or ethyl cellulose.

Silicone fluids can be added to either standard or amine-compatible silicone PSAs. The fluids act as plasticizers and lower the glass transition and the softening temperatures of the adhesive matrix, allowing the adhesive to be delivered as a hot-melt formulation rather than as the conventional silicone PSA dispersion in organic solvent. The solventless hot-melt adhesives are advantageous in that they do not require solvent removal or disposal and no special flammable ratings are required for either the material or the coating processes that use them. These adhesives can be employed for attaching devices to the skin, including transdermal drug delivery devices. However, the temperatures required for hot-melt adhesives to reach a flowable state often exceed the temperatures at which many pharmaceutical actives are thermally stable, thereby limiting their acceptance in transdermal drug delivery therapies.

Although equipment varies, constructs of both the solvated medical silicone PSA and the analogous hot-melt varieties are prepared primarily via transfer lamination. Formulation of the adhesive with additives (e.g., actives, release modulators, penetration enhancers, and cosolvents) is followed by deposition of the adhesive onto a release liner. The adhesive is then converted to its solid form either by devolatization of solvents in

the case of the solvated system or by cooling in the case of the hot-melt system. The solid adhesive is then transferred onto the substrate of choice, where it can be converted to its final form.

Typical release liners for silicone PSA are usually polyolefin films coated with either fluorosilicone or some other fluoropolymer release coating. Many release liner suppliers in the medical industry provide materials that are manufactured to some critical parameters of Good Manufacturing Practices to ensure their acceptability for health care applications.

A second type of silicone adhesive with an entirely different chemistry has recently garnered much interest in the health care industry. These adhesives are cross-linkable formulations that are designed as two-part cure systems based on a platinum-catalyzed, addition-cure reaction between functional silicone polymers: one a silicone-bonded vinyl (Si–Vi) functional polydimethylsiloxane and the second a polydimethylsiloxane with silicone–hydride (SiH) functionality. The platinum-catalyzed addition reaction can occur at room temperature or elevated temperatures. The resulting adhesive is very different from the silicone PSA in terms of property and consistency, because this silicone gel is a very soft, elastomeric silicone gel adhesive with low peel adhesion to skin and has been used effectively in wound dressing applications. Several professional wound dressings are currently available that use silicone gels as the skin-contact adhesive. Many of these dressings have been compared with traditional wound dressings and have demonstrated less pain upon removal, as well as less damage to the stratum corneum of the skin [21,22]. The need for medical dressings utilizing low-peel-adhesion adhesives that can be applied to fragile skin types without causing irritation and can then be removed from the skin without traumatizing the delicate periwound area may be highlighted by the aging population and the special needs of geriatric patients. Silicone gel technology also finds utility in the treatment of neonatal and other chronic wound sufferers.

The use of silicone gels for improving the appearance of scars has been well known for some time. In the year 2000, Posten [23] conducted a metastudy of 27 separate studies and concluded that silicone gel sheeting was superior to other occlusive dressings in the treatment and management of scars, even red and raised scars. Since the publication of the results, the market has seen a proliferation of scar therapies utilizing silicone gel sheeting.

Historically, silicone adhesive gels had to be coated and cured directly onto the backing substrate to eliminate potential chemical interaction with silicone-based release liners. This process has created significant material waste and design limitations. Recent developments have demonstrated that silicone adhesive gels can be coated and cured on a release liner, and the transfer of the silicone adhesive gels from a release liner is possible when the backing substrate has been prepared with a titanate primer [24]. Titanate primers are also known to act as adhesion promoters for silicone gels by increasing the anchorage of the gel to a given substrate. More recently, new silicone gel formulations have been created to include a hydroxy-substituted siloxane resin where priming or surface treatments of the backing substrate is not required to achieve adequate adhesion to most common medical substrates [24].

Shorter-than-desired wear times have contributed to the limited acceptance of silicone gels in the wider wound care market. One way to mitigate this issue is by the combination of an uncured silicone gel with a silicone PSA to yield a blend that displays more aggressive adhesion to steel and ostomy pouches [25]. Other recent developments have created a nontraumatic removal from skin characteristic (i.e., painless removal of adhesives from skin) while demonstrating improved skin adhesion, which should translate into longer wear times than previously achievable with traditional silicone gels [24]. Silicone tacky gels have traditionally not adhered well to wet skin, limiting their use as trauma dressings. One recent patent filing has claimed the addition of antiperspirant compounds to silicone gel formulations to create a new adhesive composition that will inhibit perspiration during cosmetic and medical uses and thus retain the skin adhesion property [26].

The trend toward skin-friendly adhesive alternatives has also received some attention in the drug delivery arena. The use of silicone tacky gels instead of silicone PSAs to optimize drug delivery devices has been suggested. The ability to formulate silicone gels at low temperatures and their characteristically low removal force from the skin have been noted as positive attributes of silicone gels in potential transdermal drug delivery applications [27]. A handful of drugs have been formulated into silicone gels with their diffusion from the silicone gel matrix measured *in vitro*. Release rate profiles of the drugs from the silicone gel matrix seem to vary based on the drug selected and the *in vitro* model selected [28]. A trade-off between the higher adhesion PSA and the lower adhesion of the silicone gels must also be acknowledged [27].

6.3 Summary

Silicone PSAs are widely recognized specialty adhesives in the PSA field. This chapter describes silicone PSA technology with emphasis on its chemistry and key components, their influence on the properties of the resulting PSAs, and major applications. The technological importance of silicone PSAs is best understood through its diverse commercial applications and its persistent and ever-increasing importance in a wide range of industries and applications.

Detailed descriptions were provided for the chemistry and peroxide-catalyzed curing of conventional solvent-based silicone PSAs, as well as the chemistry and platinum-catalyzed curing of the addition-cure silicone PSAs. The importance of silicone polymers and *MQ* siloxane resin building blocks to the properties of silicone PSAs was demonstrated. The influence of silicone polymer structure on the composition–adhesive property relations of silicone PSAs was compared, as well as its influence on rheologic properties. The preparation, characterization, and processing of silicone PSAs were also described.

Silicone PSAs are used in selected and demanding applications where organic PSAs do not meet the performance requirements. The industrial uses and applications of silicone PSAs are broadly described in three main families: masking tapes, splicing and process tapes, and high-performance insulation laminates.

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7

Hydrophilic Adhesives

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7.1 Major Trends in Hydrophilic Pressure-Sensitive Adhesive (PSA) Development

7.1.1 Application Areas Demanding the Development of Hydrophilic Pressure-Sensitive Adhesives

The vast majority of commercial PSAs are based on hydrophobic elastomers: natural or synthetic rubbers, polyisobutylene (see also Chapter 4), styrene–isoprene–styrene (SIS) triblock copolymers (see also Chapter 3), silicone (see also Chapter 6), and polyalkylacrylates[1–3] (see also Chapters 5 and 8). A common drawback of the hydrophobic adhesives is a loss of adhesion toward wet substrates[4,5] (see also *Applications of Pressure-Sensitive Products*, Chapter 7). Indeed, if adhesive material is incapable of absorbing water, any accumulation of moisture at the adhesive–substrate interface will lead to a drop in tack.[6]

In recent years PSAs have found ever-widening application in transdermal[7,8] and transmucosal[9,10] therapeutic systems for controlled drug delivery, wound dressings,[11–14] topical drug plasters,[7] and tooth whitening strips[15] and as skin-contact adhesives for the attachment of medical catheters and diagnostic electrodes[7] (see also *Applications of Pressure-Sensitive Products*, Chapters 2 and 4). Regrettably, hydrophobic PSAs have not yet been applied as broadly as was hoped in the biomedical arena. One limiting factor is a lack of adherence toward wet biological tissues that secrete moisture during the lifetime of the adhesive joint. Another limitation is an occlusive action of nonbreathable hydrophobic adhesives on human skin, resulting in skin maceration and irritation.[16,17]

Both factors limit long-term wear of adhesive patches on skin.[8] There is also the limitation of insufficient solubility of hydrophilic drugs in hydrophobic adhesives and, as a consequence, a low rate of drug delivery.

Hydrophilic PSAs have demonstrated favorable properties such as the ability to provide enhanced transdermal drug delivery due to high drug solubility in an adhesive matrix,[18] combined with the breathability of the adhesive film, which results in decreased skin irritation potential.[19] The hydrophilic adhesive is reported to provide a high value of moisture vapor transmission rate (MVTR) and allows the fluid to evaporate from the wound bed through the dressing. A high MVTR helps to promote wound healing by maintaining a friendly environment at the moist wound.

The intent of this chapter is to reveal both traditional and innovative approaches to the development of hydrophilic PSAs, focusing on the latter in more detail.

7.1.2 Improvement of Water-Absorbing Capacity of Hydrophobic Pressure-Sensitive Adhesives by Blending with Hydrophilic Absorbents

The history of hydrophilic PSA technology abounds in numerous examples of mixing hydrophobic adhesives with hydrophilic absorbents of moisture. The hydrophobic PSA therewith forms a continuous phase, whereas a disperse phase is formulated from the moisture-absorbent material. In pharmaceutical literature such adhesives are widely known as *hydrocolloid* systems (see also *Applications of Pressure-Sensitive Adhesives and Products*, Chapter 5), although in colloid chemistry the hydrocolloid is defined as a colloid system where the colloid particles are dispersed in water. Natural and synthetic hydrophilic adhesives can be employed as the absorbents of moisture: gelatin, alginates, pectins, carrageenans or xantan, cellulose derivatives (methylcellulose, hydroxypropylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose), starch and starch derivatives, polyvinyl alcohol, poly(2-hydroxyethyl methacrylate (polyHEMA), polyvinyl pyrrolidone (PVP), vinyl pyrrolidone–vinyl acetate copolymers, polyethylene glycol (PEG), polypropylene glycol, acrylic acid (AA) copolymers, etc.[20–23] Synthetic polymer absorbents, such as polyHEMA or PVP, can be either covalently cross-linked, forming a water-swellable but water-insoluble disperse phase, or uncross-linked and therefore soluble in water.[23] Some improvement in the water resistance of hydrophobic adhesives can be also achieved through the incorporation of surfactants[24] or colloid silica[25] as absorbents of moisture.

In adhesive compositions of the so-called hydrocolloid type the hydrophobic polymeric matrix provides the adhesive properties under dry conditions, whereas the dispersed hydrophilic particles absorb aqueous fluids and render the adhesive, at least to a certain extent, capable of adhering to moist surfaces, typically moist skin. Absorption is, however, not very efficient, because the hydrophilic particles are surrounded by and often enclosed in a hydrophobic matrix. An increase in hydrophilic phase content to enhance the moisture absorption capacity and to facilitate the access of liquids to the absorbent particles, on the other hand, is unavoidably accompanied by decreased adhesion as soon as the hydrophilic particles come onto the surface of the adhesive layer. This can also cause the so-called hydrocolloid adhesives to break down upon exposure to relatively large amounts of fluids. Upon contact with relatively large amounts of moisture, for

example, when the adhesive matrix is employed as a dressing on the wounds secreting large amounts of exudate, swelling of the hydrophilic polymer particles may cause the adhesive composition to lose its integrity. In turn, this results in a loss of barrier effect, and also, very often, in residues remaining on the skin upon removal of the dressing. Another common disadvantage of the so-called hydrocolloid adhesives is that they often become opaque and lose their transparency as hydrophilic absorbent particles swell in water. This property makes them inappropriate for application in wound dressings.

7.1.3 Chemical Modification of Hydrophobic Pressure-Sensitive Adhesive Polymers

7.1.3.1 Copolymerization of Polyalkyl Acrylates with Hydrophilic Monomers

The most hydrophilic PSAs from the family of hydrophobic adhesives are acrylic PSAs, and their further hydrophilization can be achieved by the inclusion of polar acrylic monomer units in their backbones. Adhesion of acrylic PSAs results from the presence in their backbones of monomer units whose homopolymers have a low glass transition temperature, T_g (Figure 7.1).[26] The T_g is one of the most important characteristics for adhesion properties of various polymers,[27,28] allowing the selection of raw materials for PSA formulation. The T_g value is informative on the suitability of a polymer as a PSA component. Typical hydrophobic PSAs possess T_g values ranging between −40 and −115°C.[27] This T_g range should be taken into account in the selection of appropriate acrylic monomers and calculation of a copolymer T_g in the development of new acrylic PSAs. Typical acrylic monomers governing the low glass transition temperature of a copolymer are *n*-butyl acrylate, *n*-octyl acrylate, and 2-ethylhexyl acrylate (2-EHA), and their homopolymers demonstrate T_g values of −54, −65, and −70°C, respectively.[26] The inclusion of hydrophilic acrylic monomers [such as AA, 2-hydroxyethyl acrylate (2-EHA), 2-hydroxypropyl acrylate, and β-acryloylpropionic acid] into the copolymer chain leads to increase T_g because corresponding homopolymers have a T_g of 106, −15, −7, and −10°C. To be a PSA, an acrylic copolymer should possess a glass transition

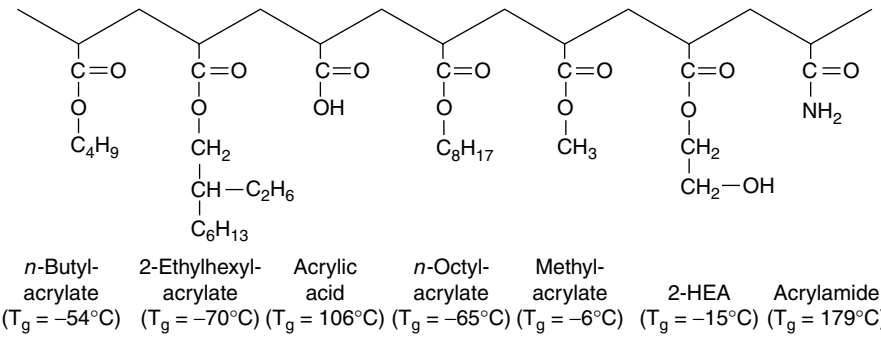


FIGURE 7.1 Architecture of acrylic PSA polymer chain. (From Czech, Z., Loclair, H., and Wesolowska, M., *Rev. Adv. Mater. Sci.*, 14, 141, 2007.)

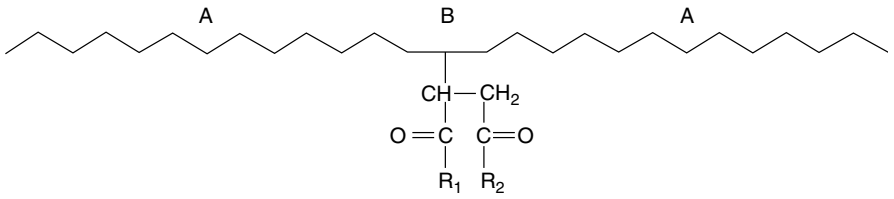


FIGURE 7.2 Chemical modification of polystyrene–polyolefin–polystyrene triblock copolymer.

temperature below −10°C, although the prerequisite T_g value is a necessary but not a sufficient condition for pressure-sensitive adhesion.[27] The full list of acrylic monomers employed for PSA formulation was presented previously by Auchter et al.[29] The approximate T_g value for copolymers can be calculated from the weight fraction of each monomer ($w_{1,2,3...}$) and the T_g of corresponding homopolymers using Fox's equation:[30]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} + \dots \tag{7.1}$$

Fox's equation is also applicable for T_g calculation in polymer blends. In this case the w_i and T_g refer to the weight fractions and glass transition temperatures of polymeric components.

The research literature reveals numerous examples of the application of such an approach to the synthesis of hydrophilic acrylic PSAs.[24,29,31–36] The results demonstrated that the water resistance of the acrylic PSAs bearing carboxyl groups in side chains were improved compared with that of the copolymers of polyalkyl acrylates.[24,36] On the other hand, the performance properties of hydrophilic PSAs are always the result of compromise between the moisture resistance and the strength of the adhesive bond.

7.1.3.2 Chemical Modification of Thermoplastic Elastomers

Attempts have been also made to obtain hydrophilic adhesives by chemical modification of other hydrophobic PSAs. As an example, U.S. Patent 7183351 by Auguste and Desmaison[37] describes a hydrophilic adhesive composition representing the blends of poly(styrene–olefin–styrene) block copolymer, poly(styrene–olefin) block copolymer, and amphiphilic ABA-type block copolymer comprising two terminal thermoplastic polystyrene (Pst) blocks and one central elastomeric block B. In the central block B a poly(ethylene-butylene) sequence bears grafted hydrophilic groups R_1 and R_2, where R_1 is $_3HC–O–(CH_2–CH_2–O)_n–$ and R_2 is $HO–(CH_2–CH_2–O)_n–$, as illustrated in Figure 7.2.[37] The molecular weight of the PEG side chains ranges from 1,000 to 8,000 g/mol. Hydrophilic adhesive composition based on this chemically modified thermoplastic elastomer contains tackifying resin, a liquid plasticizer, and water.

7.1.4 Hydrophilic Adhesives Based on Water-Absorbing and Amphiphilic Polymers

7.1.4.1 Polyvinyl Ethers (PVEs)

A fundamental description of the synthesis, properties, and application of PVE adhesives is given by Mueller[38] and Schroeder.[39] Like acrylics, these polymers can be inherently

tacky and compounding with tackifiers may not be required.[40] These adhesives, more than others, were suitable for use in medical tapes and dressings with a high water vapor permeability rate that could be equal to the rate of transepidermal water loss. These polymers, however, were expensive and subjected to oxygen degradation by chain scission. Because of these disadvantages, acrylic PSAs largely replaced PVEs.

PVEs are used both as homopolymers and as copolymers with acrylic and maleic monomers. Methyl, ethyl, isopropyl, *n*-butyl, and isobutyl ethers of vinyl alcohol are commercially available from BASF Company (Ludwigshafen, Germany). More recently, the copolymers of di-, tri-, and tetraethylene glycol vinyl methyl ethers have been synthesized and characterized.[41]

To form an adhesive composition, PVE or its copolymer can be blended with an adhesive of another type or with a nonadhesive polymer. Thus, the water-removable PSA composition has been described as containing the blends of poly(vinyl methyl ether) with a styrenic block copolymer.[42] Poly(vinyl methyl ether) comprises the major component of the PSA composition, whereas the styrenic block copolymer is a minor component that is dispersed within the PVE hydrophilic phase. The blend of poly(vinyl methyl ether) with another hydrophilic water-absorbing polymer, hydroxypropyl cellulose (HPC), resulted in only partial misciblity.[43] In contrast, the blends of poly(vinyl methyl ether) with Pst are completely miscible.[44] PVE adhesives have found pharmaceutical use in antimicrobial wound dressings[45,46] and in transdermal therapeutic systems[47] (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

7.1.4.2 Methacrylic Polyelectrolytes

In comparison with the majority of other adhesives considered in this book, methacrylic copolymers containing ionogenic functional groups in their repeat units are newcomers to the PSA market. They were originally synthesized for use as protective coatings designed to prevent drug degradation in the stomach and recently found application in the formulation of hydrophilic (or, more appropriately, amphiphilic) adhesives. Because the methacrylic copolymers are pharmaceutical grade excipients, they are currently in keen demand for the preparation of skin-contact adhesives in transdermal therapeutic systems and wound dressings.

Methacrylic polyelectrolytes are manufactured by Röhm Pharma, a part of the business unit Specialty Acrylics of Degussa AG, Darmstadt, Germany and trademarked as Eudragit® polymers. The compositions of Eudragit methacrylate copolymers used as the main components of adhesive polymer blends are presented in Table 7.1, whereas their structures are illustrated in Figure 7.3. All the Eudragit polymers are copolymers of methacrylic esters (methyl, butyl, or ethyl acrylate) with ionogenic methacrylic monomers: methacrylic acid, bearing anionic carboxyl group, and cationic tertiary or quaternary amino groups: *N*-dimethylaminoethyl methacrylate (DMAEMA) and *N*-trimethylammoniumethyl methacrylate chloride (TMAEMA).

Higher alkyl esters of AA or methacrylic acid impart rheological and adhesive properties typical of PSAs to the copolymers prepared from them. At the same time, they make the copolymers more hydrophobic and water-insoluble, regardless of the presence of highly polar and ionic functional groups. However, the change in solution pH may result in increased solubility. For this reason, in the following discussion we consider the

TABLE 7.1 Chemical Composition and Solubility of Eudragit Polyelectrolytes

Eudragit Grade	Composition, Molar Ratio						Solubility	
	MAA	MMA	EtA	BuMA	DMAEMA	TMAEMA	Alcohols[a]	H_2O
L 100	1	1					Yes	Yes, pH > 6
L 100-55	1		1				Yes	Yes, pH > 5.5
S 100	1	2					Yes	Yes, pH > 7
E 100		1		1	2		Yes	Yes, pH < 5
RL 100		10	5			1	Yes	No
RS 100		20	10			1	Yes	No

[a] Methanol, ethanol, propanol, acetone.

Note. MAA, methacrylic acid; MMA, methyl methacrylate; EtA, ethyl acrylate; BuMA, butyl methacrylate; DMAEMA, (*N*-dimethylaminoethyl) methacrylate; TMAEMA, (*N*-trimethylammonium-ethyl) methacrylate chloride.

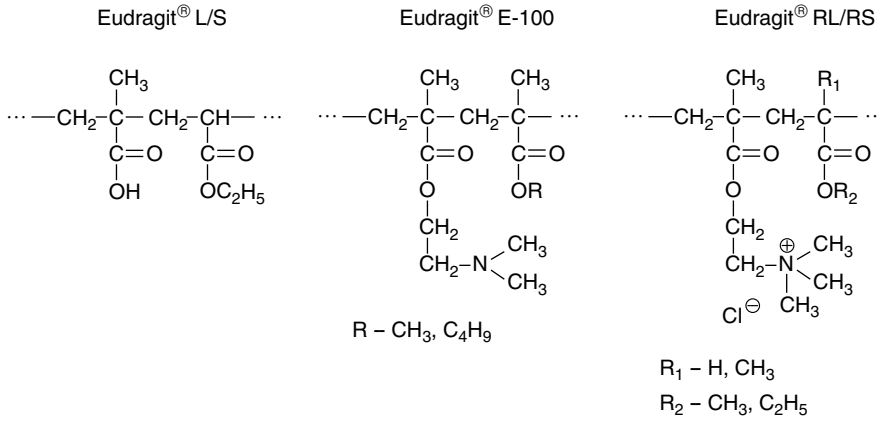


FIGURE 7.3 Chemical structure of Eudragit copolymers.

TABLE 7.2 Glass Transition Temperatures of Eudragit Copolymers

Eudragit	T_g (°C)	Reference
L-100-55	132	48
L-100-55 sodium salt	39	49
E-100	58	50
RL-100	60	51
RS-100	60	51

adhesive blends produced from the Eudragit copolymers as either amphiphilic or hydrophilic PSAs, depending on their solubility in water and values of water uptake.

Whereas typical hydrophobic PSA polymers exhibit low glass transition temperatures, this is not the case for Eudragit copolymers, whose T_g values are above 35°C (Table 7.2). To fall into the T_g range for PSAs (below −10°C),[27] these T_g values should be reduced by the addition of appropriate plasticizers. Good plasticizers for Eudragit copolymers are

triethyl citrate (TEC), acetyltriethyl citrate (ATEC), tributyl citrate (TBC), and acetyltributyl citrate (ATBC).[48,49]

Pressure-sensitive water-soluble adhesive compositions based on anionic Eudragit L-100 [poly(methacrylic acid-co-methyl methacrylate) (PMAA-co-MMA)] and L-100-55 [poly(methacrylic acid-co-ethyl acrylate) (PMAA-co-EA)] polymers were invented by Beier et al.[48] The adhesive represents the aqueous solution of the sodium salt of the film-forming polymer (FFP), Eudragit L-100 or L-100-55, with PEG-400, glycerol, or TEC employed as plasticizers. Triethanol amine can be used instead of sodium hydroxide for carboxyl group neutralization.

A water-soluble PSA composition based on the salt of cationic Eudragit E-100 [poly(*N*-dimethylaminoethyl methacrylate-co-methyl methacrylate-co-butyl methacrylate) (PDMAEMA-co-MMA-co-BMA)] is described by Petereit and Roth.[49] In this adhesive, Eudragit E-100 copolymer is mixed in a water solution with a thickener (carbonic diacids: adipic or glutaric) and with fatty acid (lauric acid), which serves as a plasticizer in the system. Water-insoluble PSA including Eudragit E-100 in nonionic form as the FFP was obtained by hot-melt mixing of Eudragit E-100, Eudragit RL-100, and Eudragit RS-100 with TBC plasticizer.[50–52] Another example of water-insoluble PSA based on Eudragit® E-100 polybase, prepared by casting-drying method, is provided by blending the Eudragit E-100, succinic diacid as a binder agent and dibutyl sebacate as plasticizer.[53] All the adhesives described[50–53] have been employed as diffusion matrices of transdermal therapeutic systems with various drugs.

Water-insoluble PSAs can be also prepared by blending cationic FFPs, Eudragit E, Eudragit RL, and RS, with anionic polymers (polyacrylic acid (Carbopol) or Eudragit L) employed as a binder.[54] Appropriate plasticizers in this case are alkyl citrate, glycerol esters, etc.

The mutual compatibility of different pairs of Eudragit polyelectrolytes has been studied.[55] Cationic Eudragit E, RL, and RS copolymers mixed with anionic Eudragit L and S polymers demonstrated the formation of visible aggregates in the range of polybase–polyacid concentrations from 30:70 to 70:30. The study performed on the other blends demonstrated that Eudragit RL and RS are compatible with Eudragit E, whereas no mutual compatibility existed among Eudragit E, L, and S copolymers. Blends of Eudragit polyelectrolytes with acrylic Durotak[53] and silicone[56] adhesives are described, as well as blends with hydroxypropyl cellulose.[57]

Eudragit copolymers represent a wide variety of convenient opportunities to formulate PSAs with properties tailored for specific applications. It is not surprising that abundant literature exists on the applications of methacrylic Eudragit polyelectrolytes as skin-contact adhesives in transdermal therapeutic systems with different drugs.[8,32,48–54,56,58–66] Drug solubility in the matrices based on Eudragit polymers is usually higher than the solubility in other (hydrophobic) adhesives and the interaction between functional groups of Eudragit copolymers and drugs often results in the inhibition of drug crystallization in the matrix.[67] Another evident benefit of Eudragit-based adhesives is their high water vapor permeability.[68–70]

It can be said with assurance that in the immediate future methacrylic polyelectrolytes based on Eudragit copolymers will become a well-accepted class of hydrophilic and amphiphilic adhesives. The most important impediment to the increasing application

of such adhesives is their comparatively low cold flow resistance, which is mainly due to the lack of Eudragit copolymers with molecular weight higher than 150,000 g/mol. A Corplex™ technology of noncovalent cross-linking of these polymers through the mechanism of interpolymer complex formation, described in Section 7.2, demonstrates the promise of overcoming this impediment.

7.1.4.3 Bioadhesives

Bioadhesion is a special case of adhesion in which the substrate is skin or a mucous membrane. Bioadhesion (and mucoadhesion) is the process whereby synthetic and natural macromolecules adhere to the skin or mucosal surfaces in the body.[10] A primary process in bioadhesion, as well as in adhesion, is a series of physicochemical interactions between functional groups of bioadhesive material and the substrate,[71,72] followed by the diffusion of bioadhesive molecules into the biosubstrate.[73] Bioadhesives are now gaining increasing attention because these polymers bind directly to receptors on the cell surface rather than to the mucus gel layer.[74] Because specific binding to the cell surface is often followed by uptake and intracellular transport, new opportunities for drug delivery are evolving.[75] Bioadhesion may, thus, enable researchers to deliver macromolecular drugs directly to specific target cells and has implications that are relevant to other fields of science, such as tissue engineering, gene delivery, and nanotechnology.[76] However, in this section we mainly focus on adhesion to skin, buccal membranes, and dental tissue, because it is precisely these areas of applications that require materials with performance properties similar to the behavior of PSAs.

Within the framework of the present discussion, bioadhesion may therefore be defined as a pressure-sensitive character of adhesion toward moist and soft biological substrates such as human skin and mucosal and dental tissues. Conventional hydrophobic PSAs adhere easily to dry skin, but they lose their tack due to skin occlusion and sweat secretion. The amount of moisture secreted by the skin is most often limited and skin-contact adhesives should possess a moderate water absorption capacity that is achievable through the hydrophilization of hydrophobic PSAs or employment of amphiphilic adhesives described previously (see Section 7.1.4.2). Mucosal and dental applications demand bioadhesives. Dry bioadhesive formulations are usually nontacky, but they achieve bioadhesion via dehydration of the local mucosal or tooth surfaces. Consequently, the first and most general requirement that should be imposed upon the bioadhesive is their hydrophilicity and ability to absorb water. Absorption of the large amounts of moisture leads inevitably to the swelling and gradual dissolution of hydrophilic polymers. In the swollen state entangled polymers usually possess a low resistance to deformation (low viscosity) and are unable to ensure suitable resistance to the subsequent dilution and shearing stress effects experienced at the site of application. Hydrogels, that is, cross-linked polymers, overcome some of these rheological requirements placed on bioadhesives. The third necessary property for bioadhesive polymers is the ability to adhere to host epithelium at the application site and hence provide residency during the therapeutic period. At the molecular level, strong adhesive contact between the bioadhesive polymer and biological adherent has been shown to result from hydrogen bonding and electrostatic interactions between complementary electron-donating and electron-accepting functional groups in the macromolecules of mucin and bioadhesive.[71,72] In particular, it was concluded that for mucoadhesion to occur, bioadhesive

polymers must have functional groups that are able to form hydrogen bonds above the critical concentration (80% for vinyl polymers), and the polymer chains should be flexible enough to form as many hydrogen bonds as possible. The latter condition can only be provided if the glass transition temperature of the bioadhesive material is at least 40–50°C below room temperature.

It is easy to perceive why the macromolecules of bioadhesive polymers bear polar functional groups in their repeat units. Early bioadhesive formulations were based on natural polymers: gelatin, carrageenan,[77] and polysaccharides such as starch,[78–80] chitosan,[14,81–84] alginate,[85] pectin, cellulose, and cellulose derivatives,[86,87] and have been used in buccal drug delivery systems due to their high biocompatibility and hydrophilicity. Synthetic polymers that have been utilized to formulate topical bioadhesive implants include poly(acrylic acid) (PAA),[71,72,88,89] PVP,[90] and polyHEMA.[90]

Synthetic polymers, PAA and PVP, in bioadhesive formulations are mainly employed in the form of covalently cross-linked hydrogels. Pharmaceutical grade cross-linked homo- and copolymers of AA and vinyl pyrrolidone are commercially available from B.F. Goodrich Brecksville, OH, USA and BASF and are generally known as Carbopol®, Noveon® (PAA),[91] and Kollidon CL® (PVP)[92] polymers. The Carbopol and Noveon cross-linked PAA are most commonly encountered in bioadhesive dosage forms. Owing to their chemical nature, these high-molecular-weight, covalently cross-linked polymers readily swell in water, providing a surface of adhesive contact with the biological substrate. The presence of a great number of carboxylic groups, which provide the ability to form hydrogen bonds, contributes to the strength of adhesive contact. Once adhered, the Carbopol resins are quite resistant to washing away. From a performance viewpoint, pH effects are highly important, because the PAA may adhere better at acidic pH levels. The pK_a of Carbopol and Noveon polymers is 6.0 $\pm$ 0.5. Above this point, the carboxylic groups are ionized to a great extent, thus reducing hydrogen bonding and the strength of adhesive contact.

The glass transition temperature of the Carbopol and Noveon polymers is 100–105°C, a value that does not fall within the range specified for PSAs. However, as the polymer absorbs water, the T_g of the swollen polymer declines and adhesion rises, displaying behavior typical of bioadhesives. Figures 7.4 and 7.5 illustrate the effect of absorbed water on probe tack adhesion for the Carbopol 974P,[93] which has found broad application as a mucoadhesive in intraoral drug dosage forms and has been used also in transdermals and topicals.

As follows from Figures 7.4 and 7.5, the amount of water uptake in the hydrogel affects both the maximum debonding stress and the work of debonding, which follow the same pattern in the course of water absorption. A relatively dry sample (containing 4 wt % absorbed water) demonstrates no adhesion. With increasing hydration, the tack passes through a maximum at 17.5 wt % water uptake and stabilizes at a mild level as the swollen hydrogel becomes softer and more compliant. Such an adhesive profile is characteristic of bioadhesives that are designed to adhere to highly moistened biological tissues. The practical work of adhesion for the Carbopol bioadhesive hydrogels is approximately 250–300 times lower than it is for acrylic PSA (Figure 7.6). This difference outlines a fundamental distinction between the bond strength of bioadhesives and PSAs. The enhancement of adhesion strength of bioadhesive hydrogels and the development of materials that bridge the gap between bioadhesives and PSAs by combining the high

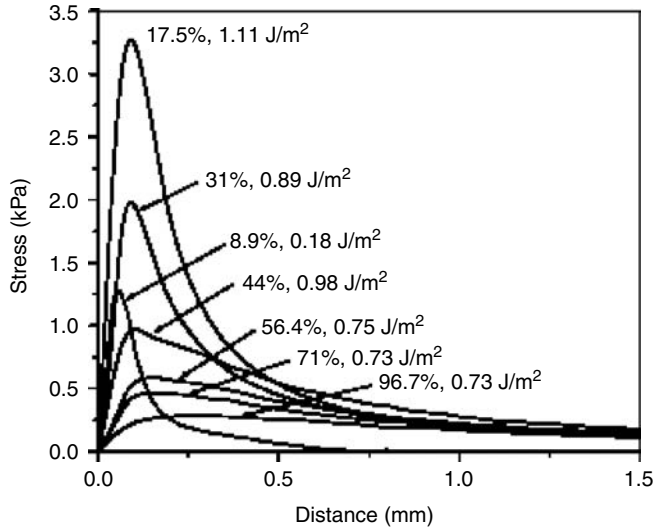


FIGURE 7.4 Probe tack curves for Carbopol® 974P bioadhesive swollen in water.[93] The values of practical work of adhesion and water sorption are indicated.

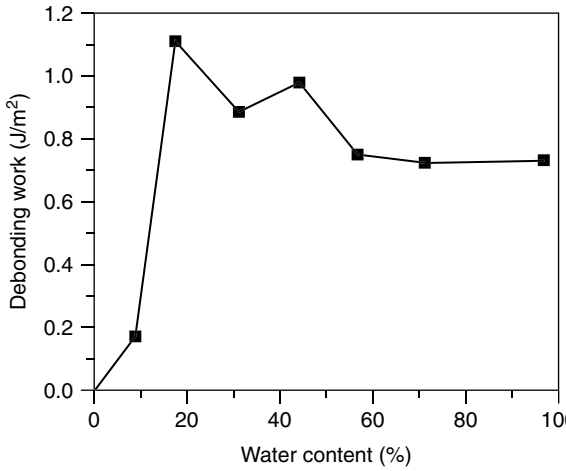


FIGURE 7.5 Effect of absorbed water on the practical work of adhesion for Carbopol® 974P bioadhesive.[93]

adhesive strength of PSAs with the ability to increase adhesion in the course of water absorption is a problem of paramount practical significance.

The attempts to resolve this problem by mixing conventional PSAs with bioadhesives, such as cross-linked PAA and PVP, are described above in Section 7.1.2. Attempts have been generally only partly successful because hydrophobic PSAs mixed with bioadhesives maintain high adhesion only in the dry state. As water uptake by the particles of a cross-linked bioadhesive exceeds 10% based on the weight of the entire two-phase composition,

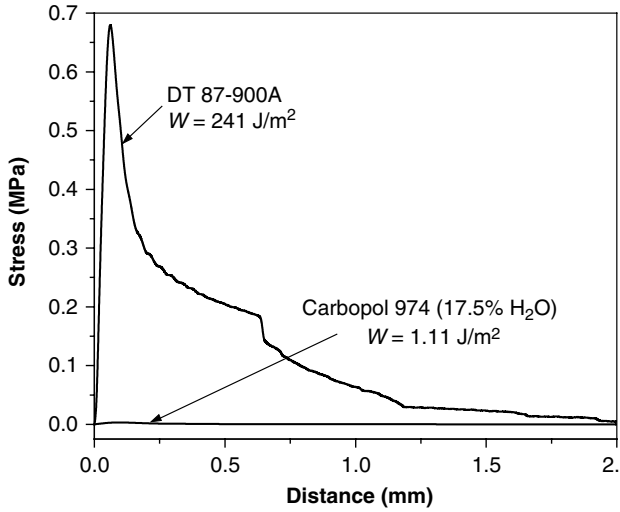


FIGURE 7.6 Comparison of probe tack curves for Carbopol® 974P bioadhesive (17.5 wt % absorbed water) and for acrylic Duro-Tak® 87-900A PSA.[93] The values of practical work of adhesion are indicated.

phase separation often occurs, indicating that the PSAs are incompatible with the swollen bioadhesives. Obtaining properties intermediate between those of PSAs and bioadhesives is, in general, not feasible within the framework of the approach based on mixing two mutually inactive polymers. Gels composed of binary interactive polymeric components could demonstrate rheological properties that are appreciably better than the sum of the individual contributions, illustrating rheological synergy between a PSA and a bioadhesive.[86] Further development of this highly productive approach is described in following sections.

7.2 Fundamentals of Molecular Design of Novel Pressure-Sensitive Adhesives and Bioadhesives

7.2.1 Molecular Structures Responsible for Pressure-Sensitive Adhesion of Polymer Blends and the Means of Their Realization

Molecular origins of pressure-sensitive adhesion are analyzed in *Fundamentals of Pressure Sensitivity*, Chapter 10. As Figure 7.7 illustrates schematically, strong pressure-sensitive adhesion appears as the high value of intermolecular cohesion energy is counterbalanced, to a certain extent, by a large free volume. The term "free volume" implies atomic-scale free volume owing to the Brownian movement of molecules and macromolecular segments, but not microscopic or macroscopic pores and holes. Cohesion and free volume are interrelated and conflicting material properties. If the cohesion is high enough, the free volume is usually small and vice versa. This deduction provides

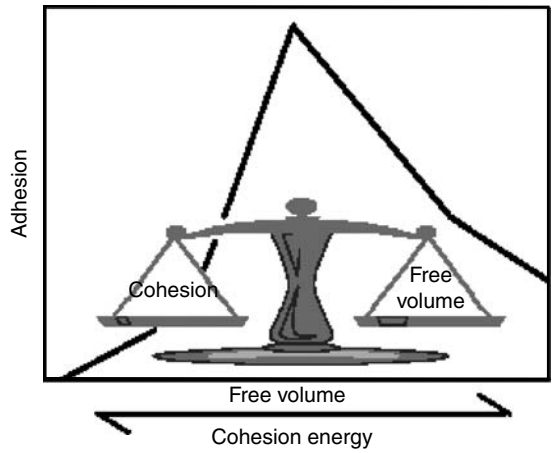


FIGURE 7.7 Schematic illustration of basic molecular properties resulting in pressure-sensitive adhesion.

the basis for the molecular design of novel PSAs. With this purpose, we should define first the molecular structures that reconcile both conflicting properties.

First, let us recall what was illustrated in Figure 10.2 of *Fundamentals of Pressure Sensitivity*, Chapter 10. In a model PSA that represents the blends of two nonadhesive polymers, high-molecular-weight PVP and oligomeric PEG, high adhesion arises from hydrogen bonding of both terminal hydroxyl groups in short PEG chains to the carbonyl groups in repeat units of PVP backbones. Second, as described above in Sections 7.1.4.2 and 7.1.4.3, adhesion may be produced by mixing two nonadhesive polymers that bear polar functional groups in the monomeric units of their backbones. These polar groups are capable of ionic, electrostatic, or hydrogen bonding to one another. It is logical to suppose that, in the blends of polymers containing complementary reactive groups, adhesion is a result of intermolecular bonding. It is generally recognized that the properties of polymeric blends are typically intermediate between those of the unblended components when the components are immiscible or partly miscible. New properties, such as adhesion, may come into existence as associating polymers in the blend form an interpolymer complex of a distinctive structure.[94–96]

Interpolymer complexes are noncovalently cross-linked three-dimensional polymer networks (gels) resulting from ionic, electrostatic, or hydrogen bonding between complementary functional groups in their macromolecules.[97,98] If both complementary polymers contain ionogenic functional groups, their association product is termed a polyelectrolyte complex. Definitions of various types of molecular interaction used in this chapter are presented in Table 7.3. A distinctive feature of hydrogen bonding between proton-donating and proton-accepting complementary groups is that both the reactive groups and the product of their interaction bear no electric charge. Electrostatic bonding is the interaction of proton-donating and proton-accepting groups, which are initially uncharged, but their interaction is accompanied by proton transfer and appearance of the charge. Finally, ionic bonding is the interaction of oppositely charged (cationic and anionic) groups with the formation of an ionic (salt) bond.

TABLE 7.3 Complementary Groups and Bonding Types

	Complementary Groups	Type of Bonding
-COOH, -PhOH, $-SO_3H$	$-NH_2$, -NHR, $-NR_2$	Electrostatic
	-OH, -C-O-C-, $-CONH_2$, -CONHR, $-CONR_2$	Hydrogen
$-COO^-$	$-NH_3^+$, $-NH_2R^+$, $-NHR_2^+$, $-NR_3^+$	Ionic
-OH	$-CONH_2$, -CONHR, $-CONR_2$	Hydrogen

-R and -Ph represent alkyl or phenyl radicals, respectively.

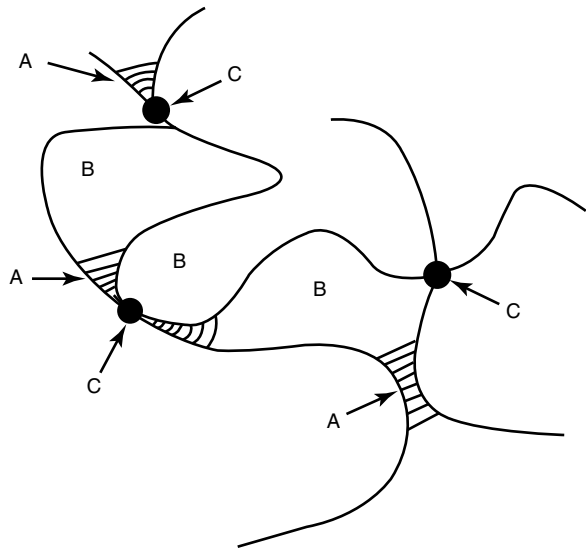


FIGURE 7.8 Schematic presentation of network structure of ladder-like interpolymer complex between film forming polymer (FFP) and ladder-like crosslinker (LLC). A: ladder-like cross-links; B: loops of polymer chains; C: polymer chain entanglements.

In interpolymer complexes the high cohesion energy is due to the formation of ionic, electrostatic, or hydrogen bonds cross-linking the polymer chains into the network (Figure 7.8A). Hydrogen bonding is substantially weaker than electrostatic or ionic bonding, whereas ionic bonds are much weaker than covalent bonds. Nevertheless, comparatively weak intermolecular bonds have an appreciable advantage over strong covalent bonds with respect to mechanical strength and adhesion of the polymer blend. Once ruptured, the covalent bond is incapable of reforming. In contrast, ionic, electrostatic, and hydrogen bonds have a temporary character and demonstrate the ability to rearrange and reform at a new place under applied mechanical or debonding stress. As a result, viscoelastic deformation and debonding of the PSA networks involving ionic, electrostatic, and hydrogen bonding can dissipate much more mechanical energy than in covalently

cross-linked adhesives.[99] Thus, the nonpermanent nature of comparatively weaker molecular interaction contributes significantly to the strength of the adhesive bond.

A large free volume within interpolymer complexes results from the defects of cross-linked supramolecular structures. As illustrated in the simplified scheme shown in Figure 7.8, such defects are, among other factors, loops (B) of polymer chains, connecting cross-linked polymer strands that represent network junctions (A). Another kind of network junctions illustrated in Figure 7.8 are the entanglements of long polymer chains (C). These entanglements serve as obstacles hindering the formation of noncovalent cross-links (A) and control the balance between high cohesion energy owing to cross-links (A) and free volume, embodied by the loops (B). Whereas the length and strength of noncovalent cross-links as well as the size of the loops depend on the nature of polymers in blend, the amount of the entanglement is a function of molecular weight and concentration of the long chain component.

Hence, the approach based on the formation of interpolymer complexes makes it possible to control the performance properties of interactive polymer blends through the manipulation of cohesion and free volume. This becomes feasible via variations of the blend composition, molecular weights of the components, concentration of polymers in a casting solution, pH and ionic strength of the solution, rate of drying, and other parameters discussed below in detail.

Only a few authors now believe that the way to the molecular design of novel hydrophilic adhesives, in many instances, is through the formation of interpolymer complexes.[100–105] Nevertheless, many well-known examples of hydrophilic PSAs and bioadhesives are in fact based on interpolymer complexes (e.g., as described in Section 7.1.4.2): the polybase–polyacid blends of cationic Eudragit E with anionic Eudragit L copolymers or with PAA (Carbopol).[54,55] The blends of cationic Eudragit E and RL/RS copolymers with carbonic diacids[49,53] may be treated as noncovalently cross-linked hydrogels, wherein the cross-linker is an oligomer-bearing reactive functional group at both ends of the short chains. Among bioadhesives (Section 7.1.4.3), examples of interpolymer complexes are PVP–PAA blends,[100,101] PAA–PEG mixtures,[102] HPC–PAA systems,[103] and chitosan–alginate complexes.[85,104] An approach based on the formation of interpolymer complexes has also found use in the development and improvement of hydrophobic PSAs. Thus, ionic interpolymer cross-linking of acrylic hot-melt PSAs may be achieved by generating an acid–base interaction between the chains of copolymers of isooctylacrylate–AA and 2-ethylhexylacrylate (EHA)–DMAEMA.[106,107] In this latter case, physical cross-linking of acrylic PSAs using acid–base molecular interaction helps to improve the rheological properties of the PSA.

Our approach to the molecular design of novel PSAs, encompassing the entire range of hydrophilicity and water-absorbing capacity (from water-soluble to amphiphilic PSAs and bioadhesives), is based on the formation of interpolymer complexes or specific favorable molecular interactions in polymer blends containing complementary functional groups. Within the framework of this approach, factors providing high cohesion include the following.

1. Covalent and noncovalent cross-linking of polymer chains into a three-dimensional network (Figure 7.8)
2. High energy of cross-linking bonds (Figure 7.8A)
3. Great network density

The factors providing increased free volume (Figure 7.8B) include the following.

1. Appreciable length and flexibility of cross-links
2. Rigidity of the long-chain polymer
3. Plasticization
4. Addition of tackifiers, where large molecules create free space in the bulk of the polymer

An advantage of the interpolymer complexation approach is that adhesive material may be obtained by mixing nonadhesive polymeric components.[108–111] It is pertinent, therefore, to consider briefly the main types of interpolymer complexes.

7.2.2 Basic Types of Interpolymer Complexes

When an interpolymer complex is formed due to hydrogen, ionic, or electrostatic bonding between functional groups of the monomer units of polymer backbones (see the scheme in Figure 7.9), the structure of the complex resembles a ladder. This type of polycomplex was first described by Zezin and Kabanov and colleagues and termed "the ladder-like interpolymer complex."[112–115] Owing to its demonstrativeness, the term ladder-like complex is widely used in polymer science.[116–122] The characteristic feature of the ladder-like complex is the formation of a network structure, wherein each network junction represents a relatively long sequence of cross-linking interpolymer bonds and is characterized by high cohesive energy. The scheme presented in Figure 7.9 illustrates that the formation of the ladder-like complex is generally accompanied by an increase in the energy of interpolymer cohesion and a decrease in free volume. Because the value of the glass transition temperature is related to the ratio of cohesion energy and free volume (see *Fundamentals of Pressure Sensitivity*, Chapter 10),[27] the T_g in polymer blends involving formation of the ladder-like complex usually demonstrates positive deviations from the simple rule of mixing established by the well-known Fox equation (Equation 7.1).[123]

The dissolution of interpolymer complexes is determined by the chemical nature of the polymer backbone structure and the nature, length, and concentration of the cross-linker. When both parent components of the ladder-like interpolymer complex, namely the FFP and the ladder-like cross-linker (LLC), are hydrophilic water-soluble polymers, the product of their interaction can be insoluble in water, but capable of swelling and it

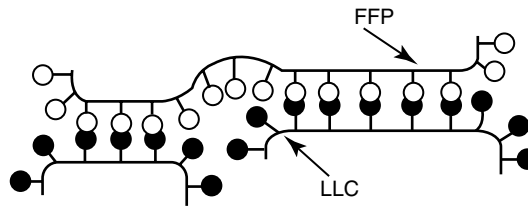


FIGURE 7.9 Schematic view of molecular structure of ladder-like interpolymer complex formed due to specific favorable interaction of the functional groups in the repeating units of a film-forming polymer (FFP) and a ladder-like cross-linker (LLC).

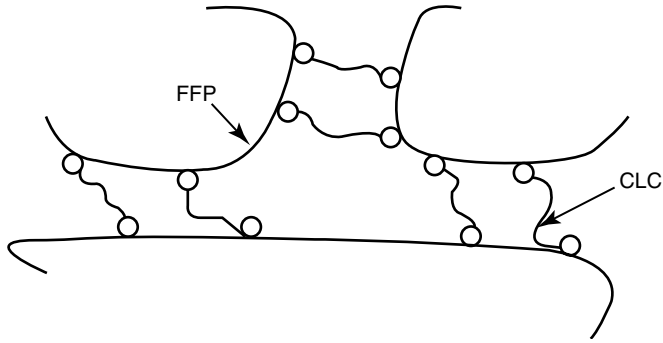


FIGURE 7.10 Schematic presentation of the supramolecular cross-linked structure of the carcass-like interpolymer complex formed due to specific favorable interaction of complementary functional groups in the repeating units of a film-forming polymer (FFP) and the terminal groups of short-chain carcass-like cross-linker (CLC).

behaves as a typical hydrogel. As a rule, water-soluble LLCs can be obtained when the water-soluble FFP is in excess with respect to the LLC.

Another type of polycomplex is formed when a macromolecule of long-chain FFP bears functional groups in the monomer units and a cross-linking oligomer contains reactive groups at the ends of the short chain (Figure 7.10). This type of complex is exemplified by the PVP–PEG system, outlined in *Fundamentals of Pressure Sensitivity*, Chapter 10.[27] Owing to appreciable length and flexibility of cross-linking oligomer chains, this type of interaction leads to the formation of large free volume. To emphasize this distinctive feature of the structure illustrated in Figure 7.10, this type of complex is called "carcass-like."[108,109,124–126] The characteristic feature of the carcass-like complexes (CLC) is that network junctions represent individual cross-linking telechelic chains, which provide comparatively low cohesive energy. It is therefore not surprising that the carcass-like complexes of hydrophilic water-soluble components are also soluble in water. Because the increase in free volume is the result of the plasticization effect, the CLC combines the functions of the noncovalent cross-linkers of polymer chains and the plasticizer.[99,124–126] In contrast to the behavior of polymer systems involving the formation of the LLCs, blending the FFP with the CLC causes a dramatic decrease in T_g and large negative T_g deviations from the rule of mixing outlined by Fox's equation (Equation 7.1).

Within the framework of the approach described below, every component of hydrophilic adhesive polymer blends is destined for a special mission to provide the tailored performance properties of the composition. Thus, the term FFP relates to a hydrophilic polymer that presents in the composition in a greater amount. The terms noncovalent cross-linker, LLC, or CLC refer to polymers that are complementary with respect to the FFP, but the amount of which in the blend is less compared with that of the FFP. The term plasticizer is used in conventional meaning and designates a low-molecular-weight or oligomeric substance that is miscible with polymer components and is capable of decreasing the glass transition temperature (T_g) and elasticity modulus of the composition. The terms tackifier and tackifying agent refer to the low-molecular weight-compounds, which enhance the tackiness of the composition. In this sense, these terms are equivalent to "the adhesion promoters."

7.2.3 Thermodynamic Principles of Interpolymer Complex Formation

The location of reactive functional groups in the macromolecules of interacting polymers has a dramatic impact upon the mechanism of interpolymer complex formation. To demonstrate this effect we must take into account the thermodynamics of complexation.

A complex is formed if the free energy of complex formation, ΔF, is zero or has a negative value,

$$\Delta F = \Delta H - T\Delta S \leq 0 \tag{7.2}$$

where ΔH is the change in enthalpy that relates to the energy of the interpolymer bond, ΔS is the change in entropy under complex formation, and T is temperature. In turn, entropy relates directly to the thermodynamic probability of the system, W, which determines the location of the molecules in space and time.[127]

$$\Delta S = R \ln W \tag{7.3}$$

If the interaction of the molecules results in generation of a molecular order, the change in entropy has a negative sign. At the same time, as Equation 7.2 demonstrates, the thermodynamic criterion of a spontaneous process is the increase in entropy, $\Delta S > 0$. This means that the formation of ordered molecular structures is only thermodynamically possible if the loss in entropy is covered by the gain in energy due to the exothermic process of interpolymer bond formation ($\Delta H < 0$).

7.2.3.1 Cooperative Character of Ladder-Like Complex Formation

Let us consider now the thermodynamics of LLC formation between two long-chain macromolecules bearing reactive groups in the repeating units of their backbones (Figure 7.11). Because the first interpolymer bond is formed due to accidental contact of complementary functional groups of FFP and LLC (Figure 7.11.a), the gain in energy occurs with the sacrifice of a single hydrogen or ionic bond formation ($\Delta H = E_{\text{bond}} < 0$), which is nevertheless accompanied by a loss in entropy ($\Delta S < 0$) due to the fixation of positions and conformations of two polymer chains in the space. This brings up the question, Where is the location of a subsequent cross-linking bond? Assume that the second bond is formed some distance

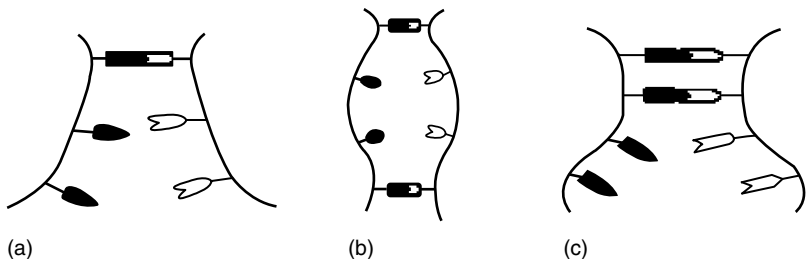


FIGURE 7.11 Schematic mechanism of ladder-like interpolymer complex formation.

away (Figure 7.11.b). In this case we will have the same gain in bonding energy ($\Delta H' = \Delta H = E_{bond} < 0$) and significant loss in entropy as a result of the fixation of long segment conformation of cross-linked polymer chains in a loop ($\Delta S' \ll 0$). Thus, the formation of the next interpolymer bond some distance away from the first one appears to be thermodynamically unfavorable.

Let us assume now that the next interpolymer bond is located adjacent to the first one (Figure 7.11.c). This situation is much more favorable because the gain in energy of the second bond formation ($\Delta H' = \Delta H = E_{bond} < 0$) does not result in a loss of entropy ($\Delta S' \approx 0$). Consequently, the free energy of the next cross-linking bond formation is less than the energy of the first one ($\Delta F' < \Delta F$). In this manner, the mechanism of ladder-like interpolymer bonding is cooperative, which follows the principle "either all or nothing" and resembles fastening a zipper. The result of LLC formation is that network junctions represent long sequences of interpolymer bonds, which are characterized by great strength and stability.

7.2.3.2 Noncooperative Mechanism of Carcass-Like Complex Formation

Figure 7.12 illustrates schematically the mechanism of CLC formation between two macromolecules of disparate chain lengths: high-molecular-weight FFP, containing reactive groups in monomer units, and oligomeric telechelic CLC, bearing reactive groups at the ends of its short chains.

When a short chain of the CLC forms a single hydrogen, electrostatic, or ionic bond with a complementary functional group in monomer units of longer macromolecule of FFPs, no cross-linking occurs and this situation is thermodynamically favorable owing to the gain in enthalpy ($\Delta H = E_{bond} < 0$) under comparatively negligible loss in entropy. The formation of the first cross-linking bond through both terminal reactive groups of the CLC results in a twofold enthalpy gain ($\Delta H = 2E_{bond} < 0$; Figure 7.12.a) and appreciable loss in entropy of the CLC chain due to the fixation of its position and conformation. The latter loss is nonetheless compensated by the increase in mobility of the FFP chain segment in the loop (Figure 7.12.a), so that the overall change in entropy tends to zero ($\Delta S \approx 0$). Let us recall that the carcass-like cross-linking of FFP leads to the plasticization of blends with an observed decrease in glass transition temperature.[126,128–131]

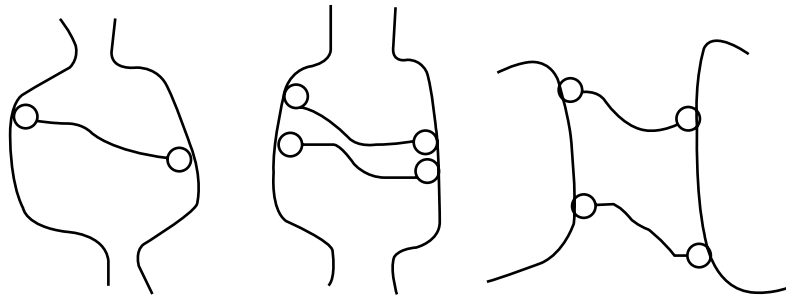


FIGURE 7.12 Schematic illustration of carcass-like complex formation.

As illustrated in Figure 7.12.b, if the subsequent cross-link is located in the immediate vicinity of the first one, the gain in enthalpy due to cross-linking bond formation ($\Delta H' = \Delta H < 0$) is accompanied by the loss in entropy of the second CLC chain, which is not made up by the increase in FFP segment mobility ($\Delta S' < 0$). Much more favorable is the situation when two neighboring cross-links are widely spaced (Figure 7.12.c). In this case, $\Delta S' \approx \Delta S \approx 0$ and $\Delta F' \approx \Delta F < 0$.

Thus, whereas the LLC network formation follows the cooperative mechanism ($\Delta F' < \Delta F < 0$, Figure 7.11.c), Carcass-like cross-linking proceeds through a noncooperative mechanism ($\Delta F' = \Delta F < 0$, Figure 7.12.c). As a result, the density and strength of the carcass-like network are much lower than in the case of complete LLC. This explains why the CLC is easily soluble, whereas the ladder-like interpolymer complex is often insoluble in water and other solvents.

An immediate consequence of the entropy compensation effect, which is observed in carcass-like network formation, is the nonequimolar stoichiometry of the carcass-like interpolymer complexes. As established previously, within a wide range of blend compositions, the amount of carcass-like PVP–PEG cross-links is 19–20% and is invariable with blend composition.[109,126,131–133] Another implication of the entropy compensation effect is the relationship between PEG chain length and the density of the carcass-like network in PVP–PEG blends. The longer the PEG chains, the greater the loss in entropy and the longer the length of PVP chain segments should be between neighboring carcass-like network junctions, that is, the sparser the density of the carcass-like network.[109,126,133]

7.3 Preparation and Performance Properties of Adhesives Based on Ladder-Like Interpolymer Complexes

7.3.1 Specific Requirements upon Preparation Method

As indicated in Section 7.2.1, in PSAs the high energy of interpolymer cohesion (cross-linking of polymer chains via ionic, electrostatic, or hydrogen bonding) must be counterbalanced by a large free volume. Owing to the cooperative mechanism of ladder-like complexation, preparation of adhesive LLCs should provide the formation of comparatively short sequences of cross-linking bonds. High cohesion energy, high density of interpolymer cross-links, and a lack of free volume, which are typical of the ladder-like network, are not favorable for pressure-sensitive adhesion. In other words, defects of the ladder-like network are in favor of adhesion.

The main factors providing the minimum length of ladder-like strands in the network complex (Figure 7.13) are as follows.

7.3.1.1 Steric Inconsistency between the Locations of Reactive Functional Groups along the Chains of Film-Forming Polymer and Ladder-Like Cross-Linker

Steric inconsistency occurs when the monomeric units containing favorably interacting functional groups in macromolecules of FFP and LLC are diluted with inert monomer

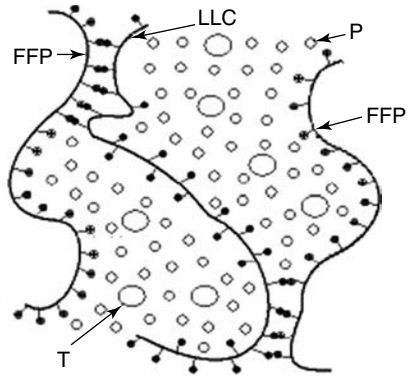


FIGURE 7.13 Schematic presentation of the structure of the ladder-like interpolymer complex formed by specific interaction of a film-forming polymer (FFP) with a ladder-like cross-linker (LLC), which may also contain a plasticizer (P) and tackifier (T). (From Feldstein, M.M., Cleary, G.W., and Platé, N.A., In: *Developments in Pressure-Sensitive Products*, 2nd ed., Taylor & Francis, New York, 2005.)

units and distributed along the backbones in an irregular manner. This can be achieved when both the FFP and the LLC are copolymers of complementary monomers with inert monomers. Although steric inconsistency is sometimes a problem, it can also be a very useful tool and may be exploited by adhesive designers to stop the formation of too-long ladder-like strands (steric protection method). In our case, this requirement is met by use of the polybase [copolymer of DMAEMA with MMA and BMA (PDMAEMA-co-MMA/BMA), Eudragit E-100] as an FFP and the polyacid [copolymer of MAA with EA (PMAA-co-EA), Eudragit L-100-55] as an LLC.[134]

7.3.1.2 Slow Addition of Diluted Solution of Ladder-Like Cross-Linker to Film-Forming Polymer Solution at High Stirring Rate and Elevated Temperature Followed by Prolonged Vigorous Stirring

If mixing of the FFP with LLC is performed in solution, the procedure of preparation should avoid local saturation with the LLC. Slow addition of the dilute LLC solution or solid LLC under vigorous stirring is useful, especially if the solid LLC is slowly soluble in the casting solution. Mixing the FFP and LLC solutions at elevated temperature leads to the formation of a homogeneous network, owing to loosening the cross-linking bonds with the increase in temperature.

7.3.1.3 Hot-Melt Mixing of FFP and LLC in the Absence of Solvent

Direct mixing of polymeric components in the solid state facilitates the formation of network defects due to the lack of molecular mobility in the mixture.

7.3.1.4 Plasticization of Ladder-Like Complex

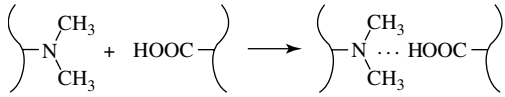
Finally, swelling of the LLC with liquid plasticizer is a most convenient and controllable tool to decrease the density of interpolymer cross-links and increase the free volume, resulting in overall enhancement of adhesion. TEC, TBC, ATEC, and ATBC served as

plasticizers for Eudragit E-100–L-100-55 blends.[134] The addition of plasticizer (P) leads to increased free volume within the interpolymer complex, as illustrated in Figure 7.13. Large cyclic molecules of a tackifier (T) create additional free volume.

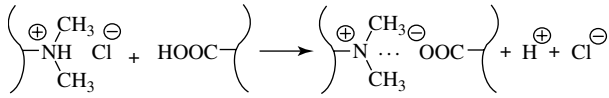
The aim of this section is to demonstrate that the adhesive and mechanical properties of polyelectrolyte LLCs may be controlled by changing their composition. The following description illustrates this approach in further detail.

7.3.2 Molecular Interaction in Polybase–Polyacid Blends

Fourier transform infrared (FTIR) spectroscopy demonstrated that amino groups of FFP are involved in strong hydrogen bonding with the carboxyl groups of polyacids (reaction of neutralization, I).[135]

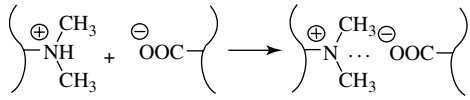


However, because the tertiary amino group of FFP is transformed into an ammonium cation by the addition of a strong inorganic acid (e.g., HCl), the reaction of exchange (II) occurs between ionized FFP and LLC, which results in the formation of ionic bonds:



This reaction has no precedent in the chemistry of low-molecular-weight compounds and is a consequence of the cooperative character of LLC formation. The existence of this type of molecular interaction has been established by the pH decrease in the course of titration of Eudragit L-100-55 polyacid by the ammonium salt of the Eudragit E-100 polybase solution (Figure 7.14).[135]

If both the tertiary amino group of the polybase and the carboxylic group of the polyacid are preliminary charged, an ionic bond is formed (III).



This reaction can be easily observed on the formation of precipitate upon mixing aqueous solutions of cationic and anionic polymers.

The energies and lengths of hydrogen, electrostatic, and ionic bonds in the Eudragit E-100–Eudragit L-100-55 system have been calculated with quantum chemical modeling.[135] As follows from the data presented in Table 7.4, the bond strength increases in passing from the H-bond (ΔE = 26.195 kJ/mol) to electrostatic bonds (in the range between ΔE = 114.00 kJ/mol and ΔE = 257.50 kJ/mol) and to ionic bonds (ΔE = 404.36 kJ/mol). The inclusion of water molecules and chlorine counterions in bonding leads to a further increase of bond energy up to 638.19 (H_2O molecule) and 644.02 kJ/mol (Cl^- anion).

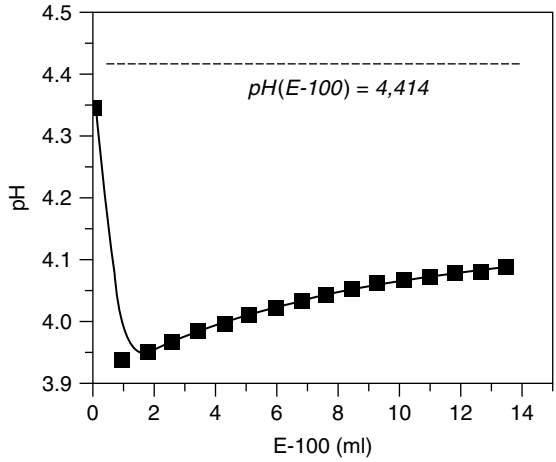


FIGURE 7.14 The curve of potentiometric titration of Eudragit L-100-55 polyacid solution (0.05 M) by 0.2 M solution of ammonium salt of Eudragit E-100 polybase. (From Kiseleva, T.I., Kostina, Y.V., Shandryuk, G.A., Bondarenko, G.N., Singh, P., and Feldstein, M.M., Proceed. 31st Annual Meeting Adhesion Society, 2008, Austin, TX, pp. 76–78. With permission.)

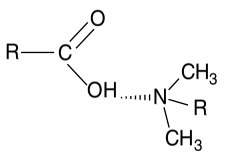
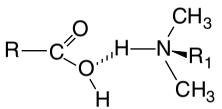
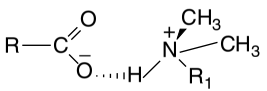
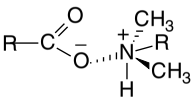
The energy of the individual bond multiplied by the average number of cross-linking bonds per ladder-like strand approximates the cohesion energy of the network (Figure 7.13) that must be counterbalanced by the free volume for adhesion to appear. Owing to the very high cohesion energy of the LLC, a large amount of appropriate plasticizer is required to render sufficient free volume and, consequently, pressure-sensitive adhesion.

7.3.3 Phase Behavior of a Polybase–Polyacid Complex

The molecular interaction in polymer blends governs the phase behavior, which in turn affects the mechanical properties, adhesion, dissolution, and swelling. The miscibility of the interpolymer ladder-like complex between Eudragit E-100 and Eudragit L-100-55 copolymers with plasticizer (TEC) is evident from the existence of a single glass transition temperature observed by differential scanning calorimetry (DSC) in the polymer blends (Figure 7.15).[134] As illustrated by the DSC data presented in Figure 7.15, the T_g of the polybase–polyacid Eudragit E-100–Eudragit L-100-55 complex is a decreasing function of TEC concentration. The relationship in Figure 7.15 reveals significant negative deviations of measured T_g values compared with those predicted using Fox's equation, which relates the T_g of the mixture to glass transition temperatures and weight fractions of individual components (Equation 7.1). The occurrence of negative T_g deviations is a sign of strong specific interactions between the polyelectrolyte complex and plasticizer (TEC).[123] Because the T_g of PSAs is normally below −40°C,[27] the relationship in Figure 7.15 implies that the plasticized Eudragit E-100–Eudragit L-100-55 complex could exhibit its best adhesive properties at TEC concentrations greater than 40 wt %.

Figure 7.16 demonstrates the effect of LLC concentration, Eudragit L-100-55, on the phase state of triple FFP–LLC–TEC blends containing a fixed amount of plasticizer

TABLE 7.4 Structure, Formation Energies, and Lengths of Hydrogen, Electrostatic, and Ionic Bonds in Polybase–Polyacid Blends

Characteristics	Model			
	1	**2**	**3**	**4**
				
ΔE (kJ/mol)	26.195	114.00	257.50	404.363
Bond length (Å)	2.55	2.41	2.21	3.41

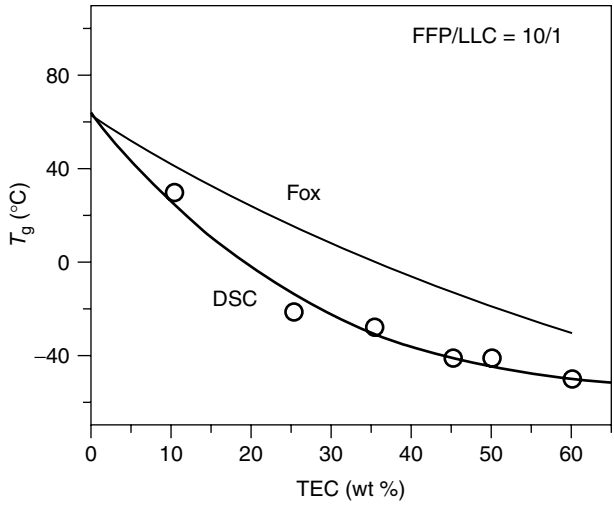


FIGURE 7.15 Dependence of glass transition temperature on plasticizer (TEC) concentration for the blends of basic FFP (Eudragit E-100) with acidic LLC (Eudragit L-100-55), FFP/LLC = 10/1.[134] Upper line refers to the relationship predicted by Fox's equation, outlining the simple rule of mixing.

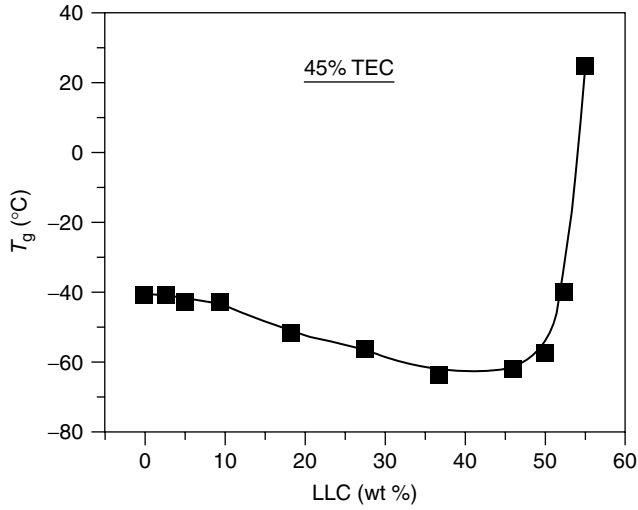


FIGURE 7.16 Effect of concentration of anionic ladder-like cross-linker, Eudragit L-100-55, on the glass transition temperature of the blends of Eudragit E-100 polybase with plasticizer, TEC. TEC content is 45 wt %. (From Kiseleva, T.I., Kostina, Y.V., Shandryuk, G.A., Bondarenko, G.N., Singh, P., and Feldstein, M.M., Proceed. 31st Annual Meeting Adhesion Society, 2008, Austin, TX, pp. 76–78. With permission.)

(45 wt % TEC). The addition of 9 wt % Eudragit L-100-55 to the Eudragit E-100 blend with 45 wt % TEC results in a negligible effect on the T_g value (decrease from −41 to −43°C). Further incorporation of LLC up to 37 wt % leads to significant T_g reduction (−64°C). At concentrations of Eudragit L-100-55 higher than 46%, the T_g increases dramatically. To gain insight into such T_g behavior, let us recall that the value of the glass transition temperature increases directly with cohesion energy and decreases with free volume (see *Fundamentals of Pressure Sensitivity*, Chapter 10).[27] The implication of data in Figure 7.16 is that at small concentrations of noncovalent cross-linker the contributions of the increase in both cohesion energy due to ladder-like strands and free volume as a result of loops formation are counterbalanced, whereas at higher LLC concentrations the free volume within polymer chain loops filled with plasticizer dominates the contribution of interchain cross-links.

7.3.4 Effect of the Composition of Ternary Polybase–Polyacid Blends with Plasticizer on Mechanical Properties

Let us consider now how the phase behavior of Eudragit E-100–Eudragit L-100-55–TEC blends affects their mechanical properties. As illustrated in Figure 7.17, the tensile stress–strain curve under uniaxial drawing of uncross-linked blend of Eudragit E-100 with 25% plasticizer (TEC) is typical of such viscoelastic liquids as the entangled blends of linear polymers or uncured rubbers. The addition of a small amount of LLC Eudragit L-100-55 (FFP/LLC = 10/1) results in a solid-like deformation behavior, which is inherent in

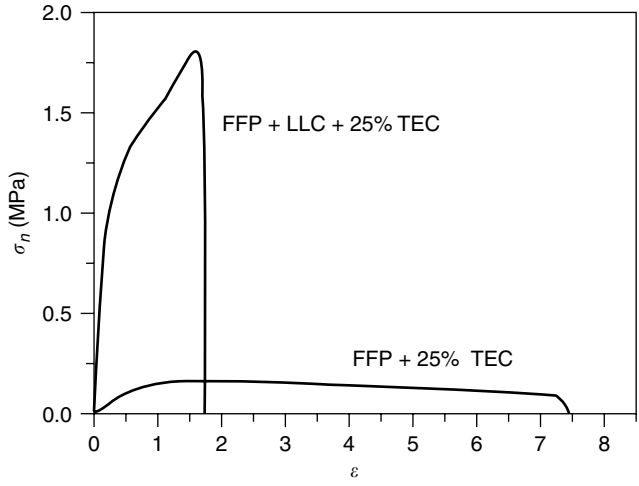


FIGURE 7.17 Nominal stress–strain curves for uniaxial drawing of the mixture of FFP with 25 w/w % TEC and ladder-like interpolymer complex ([FFP]:[LLC] = 10:1) plasticized with the same amount of TEC. Drawing rate is 20 mm/min. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

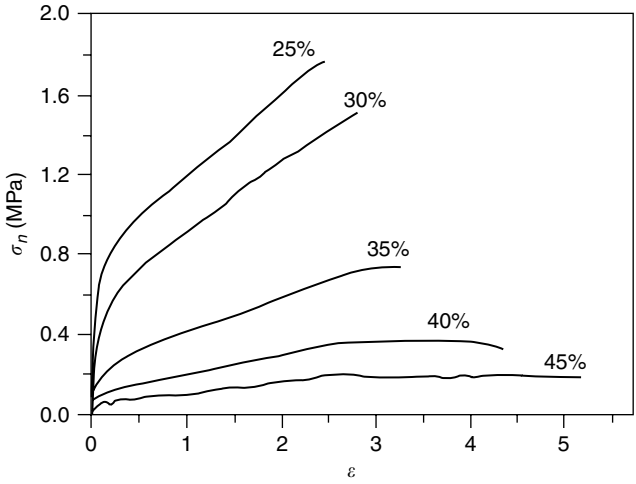


FIGURE 7.18 Effect of plasticizer concentration on tensile stress–strain curves of Eudragit E-100–Eudragit L-100-55 blends, FFP/LLC = 10/1. TEC content is indicated. (From Kiseleva, T.I., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein M.M., in preparation. With permission.)

strongly cured elastomers. Mixing FFP with LLC in a ratio of [FFP]:[LLC] = 10:1 leads to a dramatic increase in the value of ultimate tensile stress (6.6 times larger), whereas the value of maximum elongation at break decreases by a factor of 4.3 (Figure 7.17). The former value may be regarded as an indirect measure of the cohesive strength of stretched material, whereas the latter relates to the free volume.[99]

Figure 7.18[136] illustrates the effect of plasticizer concentration on the tensile properties of LLCs. As illustrated in Figure 7.18, the stress–strain curves for the Eudragit E-100–Eudragit L-100-55–TEC films are similar in shape to those observed for cured elastomers. This is manifested by high ultimate strains (ε_b) typical for rubbers, as well as the absence of ductile or "plastic flow" regions characteristic of plastic deformation. Ultimate strain or relative elongation is defined as the increase in sample length at break point divided by the original length of the sample. TEC is a good plasticizer of Eudragit E-100–Eudragit L-100-55 blends. With the increase in plasticizer content, the values of both ultimate tensile stress and the work of viscoelastic deformation up to break (area under stress–strain curve) decline, whereas maximum elongation increases.

In this manner, varying the composition of FFP–LLC blends with plasticizer renders easy tuning of mechanical properties. The ultimate strength and ductility of the blends are such that they can be useful in many practical applications.

7.3.5 Adhesive Properties

7.3.5.1 Effect of Ladder-Like Cross-Linker

The probe tack profiles in Figure 7.19 are informative for the mechanism of debonding process. The PSAs are known to couple the properties of liquid-like and solid-like materials and the shape of the stress–strain curves illustrates this dualism. In probe tack

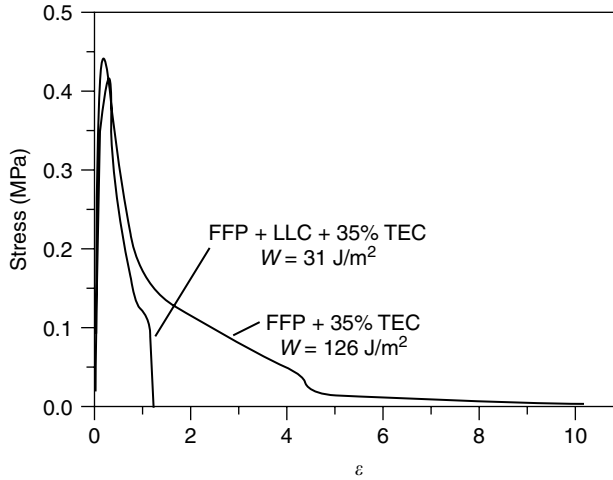


FIGURE 7.19 Effect of LLC content on probe tack stress–strain curves of the blends of film-forming polybase (Eudragit E-100) with polyacid LLC (Eudragit L-100-55). (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

curves, the liquid-like behavior relates to the material capability of developing very high values of maximum elongation ($\varepsilon \approx 10$–40) under comparatively low levels of applied detaching stress (much lower, 0.1 MPa). In contrast, solid-like behavior is evident when debonding occurs at relatively small values of maximum elongation ($\varepsilon < 1$) and is provided by high values of debonding stress. As follows from the curves in Figure 7.19, the ladder-like noncovalent cross-linking of FFP (Eudragit E-100) with Eudragit L-100-55 results in a dramatic change in debonding mechanism, from that typical of conventional PSAs (observed for plasticized Eudragit E-100) to one more solid-like, featured for ternary Eudragit E-100–Eudragit L-100-55–TEC blends.

In probe tack curves, the stress peak relates to the cavitation of the adhesive material under detaching tensile force.[28,137,138] The major factor providing dissipation of a great amount of energy in the course of debonding PSAs is the fibrillation of the adhesive film, which is observed by the appearance of a plateau on stress–strain curves. Adhesive joints of solid adhesives fail predominantly via the mechanism of cavitation that is not followed by fibrillation. The typical shape of their probe tack stress–strain curves is a symmetric peak. In the probe tack experiment, the maximum stress is generally considered a measure of tack, the value of plateau stress characterizes the cohesive strength of fibrils, and the area under the stress–strain curve relates to the total amount of mechanical energy needed for adhesive bond failure. In this way, the latter value is a measure of adhesive strength (practical work of adhesion, W).

As illustrated in the stress–strain curves presented in Figure 7.19, a binary blend of Eudragit E-100 containing 35 w/w % plasticizer TEC and no cross-linker is a highly tacky fluid that debonds cohesively at relatively high values of elongation, leaving significant

amount of adhesive at the surface of the probe. Mixing the FFP with complementary LLC Eudragit L-100-55 in a ratio of [FFP]:[LLC] = 10:1 leads to an immediate change in the debonding mechanism from cohesive to adhesive. Ladder-like cross-linking of FFP decreases the work of debonding from 126 to 31 J/m^2. Thus, domination of the cohesion interaction over free volume space is produced by the ladder-like cross-linking of FFP, which affects the adhesion properties.

7.3.5.2 Impacts of Plasticizer and Tackifier

As follows from the probe tack curves illustrated in Figure 7.20, plasticization of Eudragit E-100–Eudragit L-100-55 blend with TEC causes transition of the debonding type from solid-like to fibrillar and increased adhesion (Figure 7.21).[134] The blend containing 25% plasticizer exhibits solid-like behavior and an adhesive mechanism of debonding. With the increase of TEC concentration up to 35%, the value of peak stress increases, achieving its maximum at 35–45% TEC, and the appearance of a plateau on the stress–strain curve signifies the process of fibrillation of the adhesive. The work of debonding goes through a maximum at 45–50% TEC (Figure 7.21). These blends demonstrate the best adhesion. Further increase in plasticizer content leads to a gradual decrease of both tack (maximum stress, Figure 7.20) and the practical work of adhesion (Figure 7.21). Whereas the LLC plasticized with 50% TEC reveals the adhesive mechanism of debonding, observable by a sharp drop in stress at the moment of adhesive bond failure, the blend containing 60 wt % TEC debonds cohesively, leaving adhesive on the probe. In this case, the stress tends gradually to zero as the fibrils are ruptured (Figure 7.20).[134]

Plasticizer hydrophilicity appreciably affects the adhesive properties of the interpolymer complex (Figure 7.22).[134] The higher the plasticizer hydrophilicity, the higher the

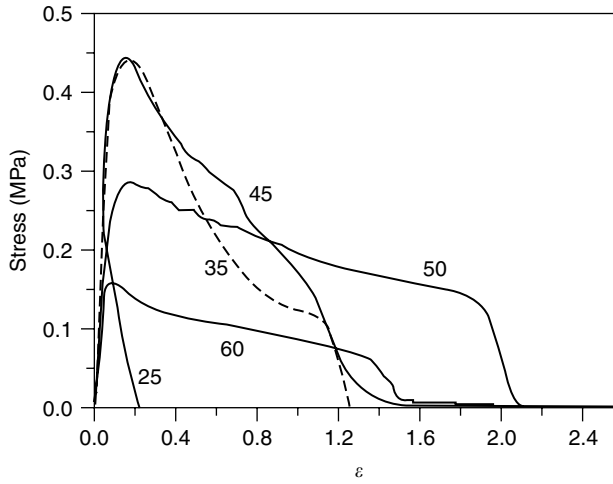


FIGURE 7.20 Effect of plasticizer (TEC) concentration on probe tack stress–strain curves of blends of FFP Eudragit E-100 polybase with LLC Eudragit L-100-55 polyacid (FFP:LLC = 10:1). TEC concentrations are indicated. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

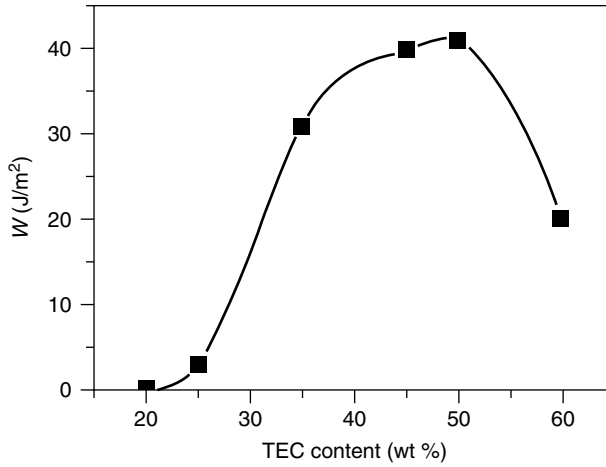


FIGURE 7.21 The work of adhesive debonding as a function of plasticizer concentration for ladder-like complex of Eudragit E-100 with Eudragit L-100-55; FFP:LLC = 10:1. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

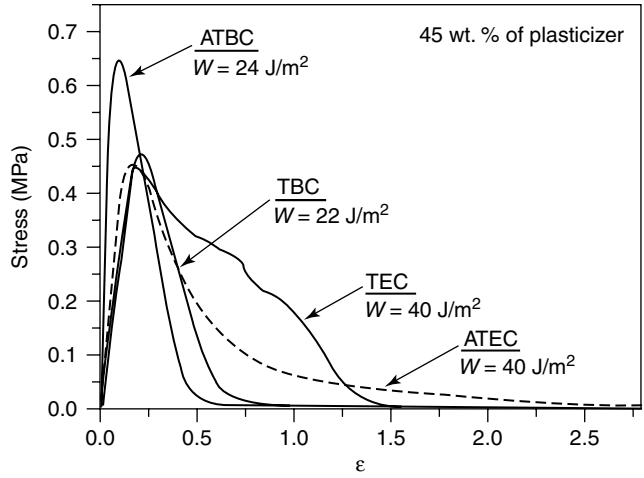


FIGURE 7.22 Impact of plasticizer hydrophilicity upon probe tack curves of the blends composed of the polybase (Eudragit E-100)–polyacid (Eudragit L-100-55) ladder-like complex (10:1). (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

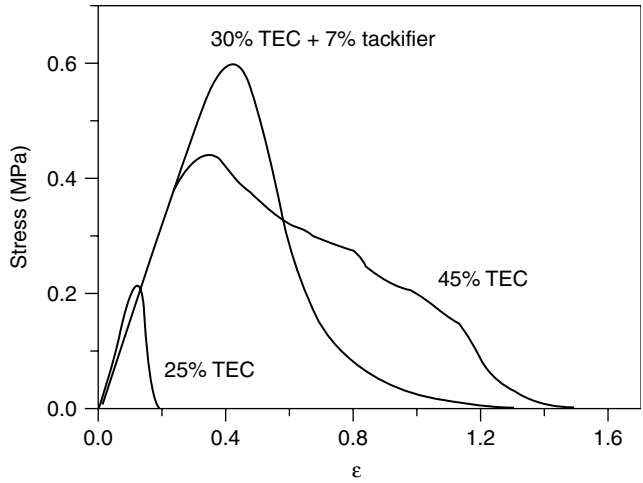


FIGURE 7.23 Comparative effects of plasticizer (TEC) and tackifier (glycerol ester of tall oil rosin) on probe tack stress–strain curves of adhesives based on the ladder-like complex of Eudragit E-100 and Eudragit L-100-55 copolymers (10:1). (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304.)

adhesion. The compositional behavior of the practical work of adhesion follows the pattern demonstrated by plasticizer hydrophilicity, which increases in the order ATBC < TBC < ATEC < TEC.

Owing to the presence of an appreciable amount of hydrophobic monomer units in cationic Eudragit E-100 and anionic Eudragit L-100-55 copolymers, adhesives based on acid–base polymer complexes are miscible with nonpolar tackifiers (rosins) and conventional acrylic PSAs employed in the adhesive industry. As illustrated by the probe tack curves in Figure 7.23, the addition of tackifier (glycerol ester of tall oil rosin) improves the tack of plasticized LLC significantly.[134]

7.3.5.3 Effects of Bonding Type and Nature of Noncovalent Cross-Linker

Partial ionization of polybases or polyacids in the blend achieved with the addition of a strong inorganic acid (HCl) or base (NaOH) also improves the adhesive properties and changes the mechanism of debonding from fibrillar to solid-like (Figures 7.24 through 7.26).

The implication of probe tack data illustrated in Figures 7.24 through 7.26 is that the adhesive properties are affected by a mechanism of specific interaction between the components of the interpolymer complex (hydrogen or ionic bonding), which governs the structure of the complex and determines the balance between cohesion energy and free volume. In aqueous media, the electron-donating amino groups of Eudragit E-100 are capable of forming hydrogen bonds with the proton-donating carboxylic groups of Eudragit L-100-55 (see Section 7.3.2). Treatment of Eudragit E-100 in aqueous solution by HCl causes partial ionization of the polybase and the formation of ammonium

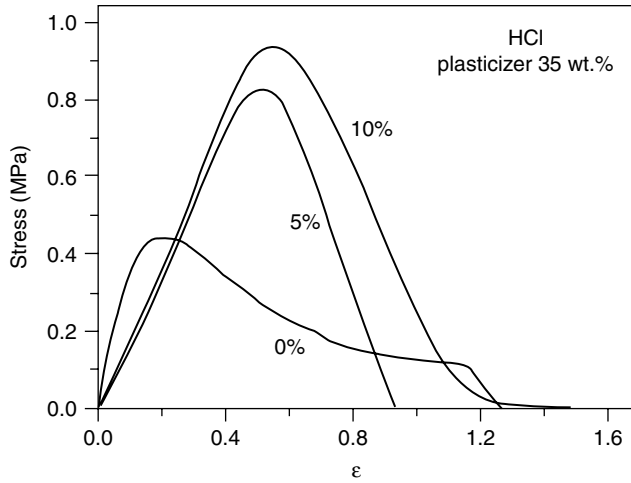


FIGURE 7.24 The effect of partial ionization of amino groups in Eudragit E-100 copolymer on probe tack curves of a ladder-like interpolymer complex plasticized with TEC. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

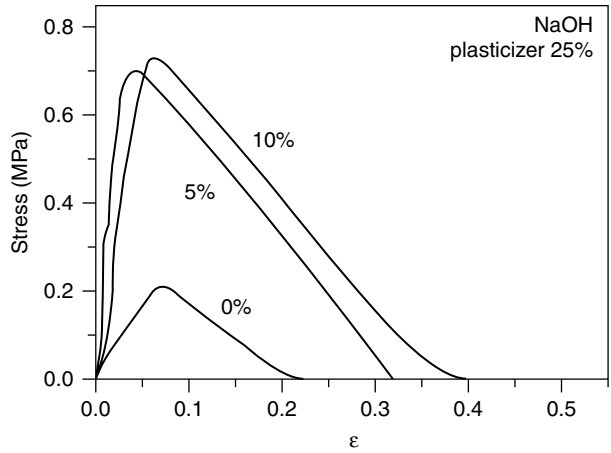


FIGURE 7.25 The effect of partial ionization of LLC by NaOH solution on the tack of polybase Eudragit E-100–polyacid Eudragit L-100-55 adhesive containing 25 wt % plasticizer TEC. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

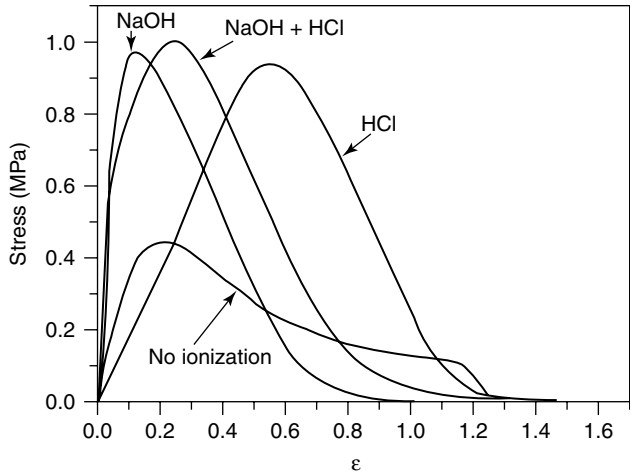


FIGURE 7.26 Probe tack stress–strain curves for the polybase Eudragit E-100–polyacid Eudragit L-100-55 adhesive containing 35 wt % plasticizer TEC under 10% ionization of FFP and LLC and for the complex formed between partly ionized polymer components at 10% degree of ionization. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

cations, which can interact with the carboxyl groups of PMAA-co-EA LLC through the exchange reaction (see Reaction II, Section 7.3.2). Ionic bonds are stronger than hydrogen bonds, and as the data presented in Figure 7.24 illustrate, the increase in the energy of interpolymer bonding leads to the increase in both the energy of cohesion and adhesion. This allows us to suppose that the free volume in the LLC involving ionic bonds increases accordingly. Electrostatic repulsion of cationic ammonium groups in ionized Eudragit E-100 leads to the increase in free volume.[134]

Partial neutralization of the carboxylic groups of LLC, polyacid Eudragit L-100-55, by treatment with NaOH solution results in the formation of carboxylate anions that are unable to interact with neutral amino groups of FFP, Eudragit E-100, and therefore do not contribute to the increase in cohesion energy. However, electrostatic repulsion between these anions increases the free volume. As a result, adhesion increases, illustrated by probe tack data in Figure 7.25. Finally, the combined effect of ammonium cations in FFP and carboxylate anions in the LLC enhances adhesion, as evidenced by the data illustrated in Figure 7.26.

Eudragit E-100 and Eudragit L-100-55 are not unique FFP and LLC suitable for the preparation of adhesives based on the mechanism of LLC formation. As Figure 7.27 illustrates, replacement of Eudragit E-100 by the copolymer of maleic acid with methylvinyl ether, PMA-co-MVE, increases adhesion appreciably, implying that the approach illustrated in this section has a general character.

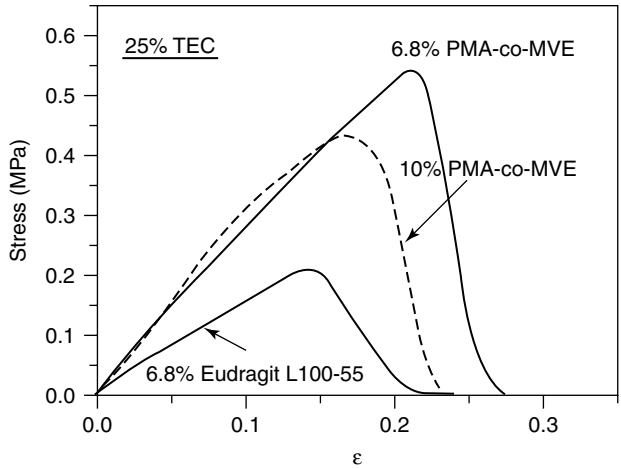


FIGURE 7.27 Probe tack behavior of interpolymer complexes of Eudragit E-100 film-forming polymer with the ladder-like cross-linkers of different hydrophilicity and hydrogen-bonding capability: Eudragit L-100-55 (6.8 wt %) and PMA–co–MVE. The content of plasticizer TEC in blends is 25 wt %. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

7.3.6 Water-Absorbing Capacity and Solubility in Water

As illustrated by the data in Figure 7.28, FFP–LLC complex formation leads to a loss in solubility of the polymer blend in water (expressed in terms of sol fraction, SF) and a comparatively small reduction of swell ratio (SR), defined as the weight of the material in a swollen state divided by the dry weight of its gel fraction.

The SR is a fundamental characteristic of cross-linked polymeric gels that relates to the density of network junctions. The lower the SR value, the higher the density of the ladder-like network.[139] The increase in LLC concentration (i.e., the decrease in FFP:LLC ratio) makes the ladder-like network denser and significantly decreases both the solubility (SF) and the swelling (SR) of the EudragitE-100–Eudragit L-100-55 interpolymer complex. As Figure 7.29 illustrates, the density of cross-links, expressed in terms of the SR value, controls the solubility of the ladder-like interpolymer complex. The reduction of both values is more pronounced at comparatively small LLC concentrations (below 40 wt %). Further increase in LLC content has only a negligible effect on dissolution and swelling properties.[134]

The swell ratio and the content of soluble fraction in the LLC of Eudragit E-100 with Eudragit L-100-55 depends on plasticizer (TEC) concentration (Figure 7.30). Also, the higher the hydrophilicity of the plasticizer, the greater the SF (Figure 7.31) and SR values of the blends. The 10% ionization of Eudragit E-100 and Eudragit L-100-55 polymers increases their solubility in water. This behavior is also typical of their LLC containing 25 wt % TEC that exhibits a solid-like mechanism of debonding in a probe tack test (Figure 7.20). However, the blend with 35 wt % TEC, which reveals transitional probe tack profile from solid-like to fibrillar type of adhesive bond failure, demonstrates

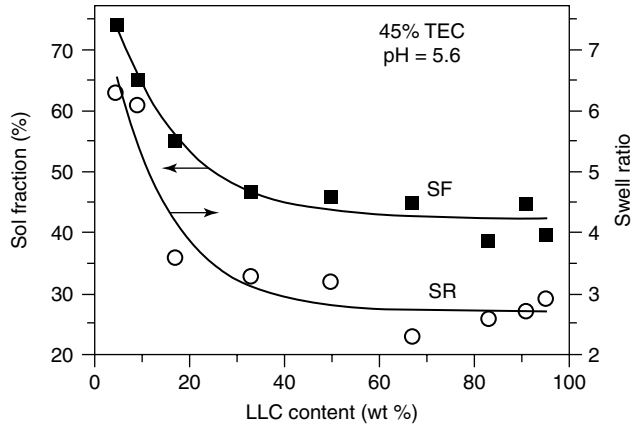


FIGURE 7.28 Effect of LLC concentration on solubility (SF) and swelling (SR) of Eudragit E-100 blend with Eudragit L-100-55 in water, pH 5.6. TEC content is 45 wt %. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

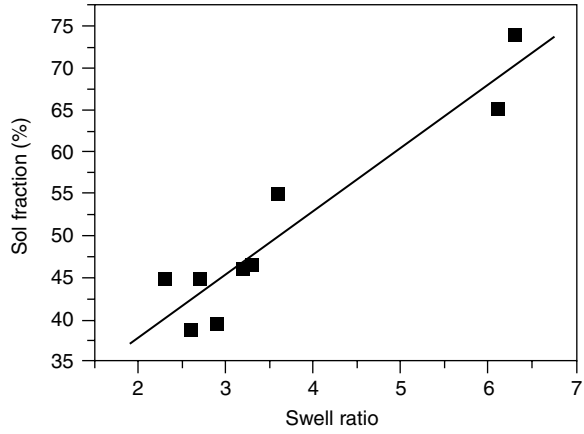


FIGURE 7.29 The content of the soluble fraction in the Eudragit E-100–Eudragit L-100-55 complex as a function of the value of swell ratio; pH 5.6. The concentration of the plasticizer (TEC) is 45 wt %. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

decreased solubility with 10% ionization of DMAEMA amino groups and an insignificant effect with the ionization of MAA carboxyl groups (Figure 7.32).

In full agreement with the established mechanism of FFP–LLC interaction (see Section 7.3.2), 10% ionization of amino groups in FFP causes the drop in SR, whereas the ionization of carboxyl groups of the LLC does not contribute to the SR value or to the

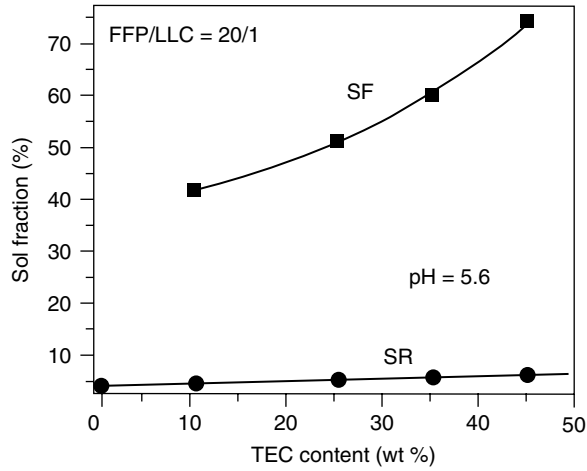


FIGURE 7.30 Effect of plasticizer concentration on solubility and swelling properties of the ladder-like polyelectrolyte complex of Eudragit E-100 polybase (FFP) with Eudragit L-100-55 polyacid (LLC). The FFP/LLC ratio is 20:1. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

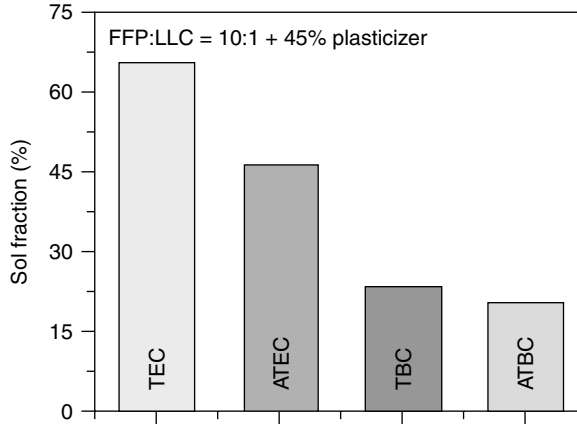


FIGURE 7.31 Effect of plasticizer hydrophilicity on the dissolution of polymer blends in water; pH 5.6. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

density of the interpolymer network (Figure 7.33). For the complex containing 25 wt % plasticizer, no effect of 10% ionization of amino and carboxyl groups on SR value has been observed.[134]

Replacement of Eudragit L-100-55 for a more hydrophilic copolymer of maleic acid with methylvinyl ether, PMA-co-MVE, increases dramatically both the swell ratio

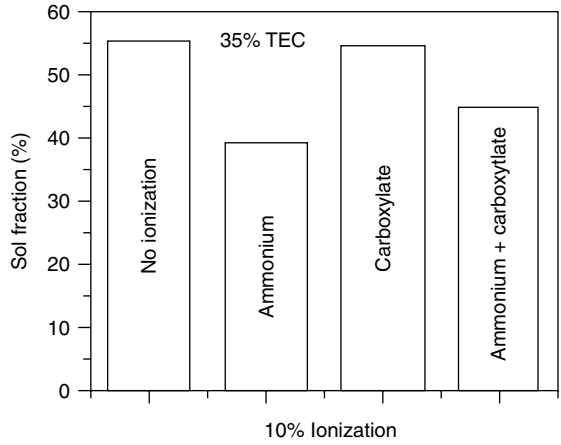


FIGURE 7.32 Sol fraction of plasticized Eudragit E-100 interpolymer complex with Eudragit L-100-55 at 10% ionization of amino and carboxyl groups of FFP and LLC. FFP:LLC ratio is 10:1; pH 5.6. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

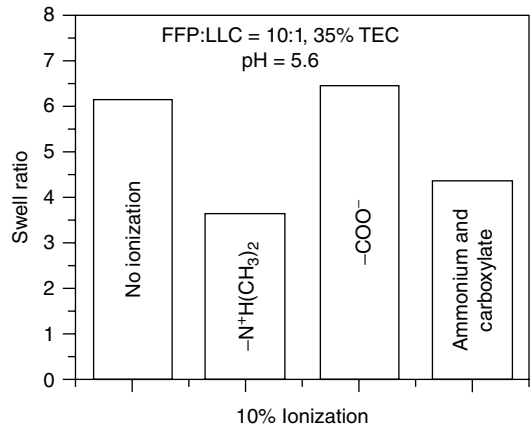


FIGURE 7.33 Swell ratio of plasticized Eudragit E-100 interpolymer complex with Eudragit L-100-55 at 10% ionization of the amino and carboxyl groups of FFP and LLC. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

(Figure 7.34) and the sol fraction of their blends with Eudragit E-100. The content of soluble fraction in this case is 88 and 49% for the complexes with 6.8 and 10% PMA-co-MVE.[134]

In this way, the adhesive properties of polymer blends can be easily manipulated by changing the relative composition of various copolymers in the blends. Owing to the

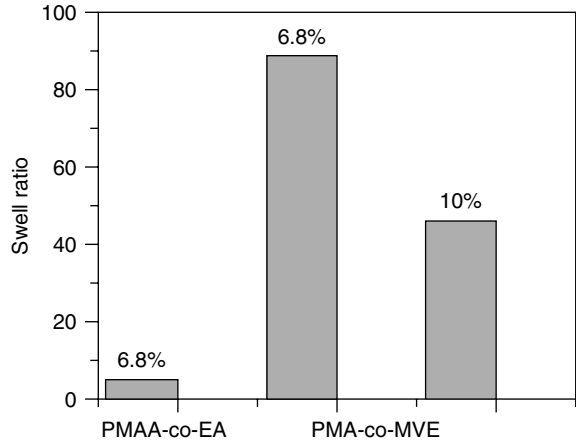


FIGURE 7.34 Swell ratio of Eudragit E-100 blends with different amounts of ladder-like cross-linkers: Eudragit L-100-55 and PMA-co-MVE. (From Kiseleva, T.I., Novikov, M.B., Shandryuk, G.A., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., Proceedings of the 29th Annual Meeting of the Adhesion Society, 19–22 February 2006, Jacksonville, FL, pp. 302–304. With permission.)

presence of polar (ionic) and nonpolar groups in the copolymers, the materials based on electrostatic interpolymer complexes may be classified as "amphiphilic" adhesives. Such adhesives are compatible with both hydrophilic and hydrophobic drugs and can be developed for diverse applications in various industries, particularly in drug delivery. The composites based on such interpolymer complexes are now available as Corplex adhesives from Corium International (Menlo Park, CA).[140]

7.4 Performance Properties of Adhesives Based on Carcass-Like Polymer–Oligomer Complexes

7.4.1 Brief Introduction to the Formation Mechanism, Stoichiometry, Phase Behavior, and Basic Physical Properties of Poly(*N*-Vinyl Pyrrolidone)–Poly(Ethylene Glycol) Complex

The typical and most thoroughly studied example of the CLC is the product of hydrogen bonding between proton-accepting carbonyl groups in repeat units of high-molecular-weight PVP and proton-donating hydroxyl groups at both ends of the PEG short chains (see *Fundamentals of Pressure Sensitivity*, Chapter 10).[27] Readers may already be aware of the structure and some of the properties of PVP–PEG blends. In the unblended state, both glassy PVP and liquid oligomeric PEG ranging in molecular weight from 200 to 600 g/mol are not tacky, but when mixed in a certain ratio (36 wt % PEG-400) they demonstrate pressure-sensitive adhesion (see *Fundamentals of Pressure Sensitivity*, Chapter 10).[27] Considering the structure and properties

of PVP–PEG blends that possess different levels of pressure-sensitive adhesion, in *Fundamentals of Applied Pressure Sensitivity*, Chapter 10, we established a quantitative structure–property relationship and gained insight into the molecular origins of pressure-sensitive adhesion.[27] Pressure-sensitive adhesion of PVP–PEG blends has been shown to be the result of the CLC formation and nonpermanent cross-linking of longer PVP chains into a labile network by hydrogen bonding via shorter PEG chains.[27] The high cohesive strength of the PVP–PEG network is a consequence of hydrogen bonding, whereas the large free volume results from the appreciable length and flexibility of shorter PEG chains, which increase the space between neighboring PVP macromolecules. In *Fundamentals of Pressure Sensitivity*, Chapter 10,[27] we compared the compositional behaviors of the free volume and adhesion in PVP–PEG blends and phase state, diffusion, viscoelastic properties, and adhesion of the PVP–PEG adhesives with those of conventional PSAs. Comparison of the relaxation properties of the PVP–PEG model PSA and typical hydrophobic adhesives allowed us to establish relaxation criteria for pressure-sensitive adhesion, which are described in *Fundamentals of Pressure Sensitivity*, Chapter 11.

The mechanism of molecular interaction, phase behavior, and the structure and physical properties of the PVP–PEG blends are described in a range of research papers that were recently reviewed.[126] In this section we discuss adhesive and mechanical properties of PVP–PEG blends containing different amounts of water absorbed as a vapor from the surrounding atmosphere. In contrast with the behavior of ladder-like interpolymer complexes that are formed due to cooperative interaction between complementary macromolecules, the noncooperative mechanism of CLC formation leads to adhesive materials demonstrating dissimilar performance properties.

7.4.2 Effects of Plasticizer and Absorbed Water on Mechanical Properties

In the course of adhesive joint failure, adhesive film is stretched under applied detaching (for instance, peeling) force. For this reason, the tensile properties of PSAs, especially at large deformations, are very important to gain insight into their adhesive performance. Detailed analysis of these properties for a PVP–PEG system was presented in a recent publication.[99]

Under comparatively high concentrations of CLC (PEG) and absorbed water, the stress–strain curves have a form characteristic of viscoelastic liquids and ductile, uncured rubbers (Figures 7.35 and 7.36). At lower PEG and water content, they become more like slightly cross-linked elastomers that deform tightly. The most remarkable feature of the uniaxial drawing of the PVP–PEG hydrogen-bonded network is that the ductile–tight transition occurs very abruptly, within a very narrow range of PEG and water concentration (36–34% PEG, 6.5–4.5% water). The narrow range of the ductile–tight transition in Figures 7.35 and 7.36 corresponds well to the rapid transition from a tacky, fibrillar failure to a nontacky and nonfibrillar failure in the probe tack test.[141] Both PEG and water are good plasticizers for FFP.

Figures 7.35 through 7.38 compare the effects of PEG-400 and water on the tensile stress–strain curves of PVP–PEG blends. The addition of both plasticizers, PEG and

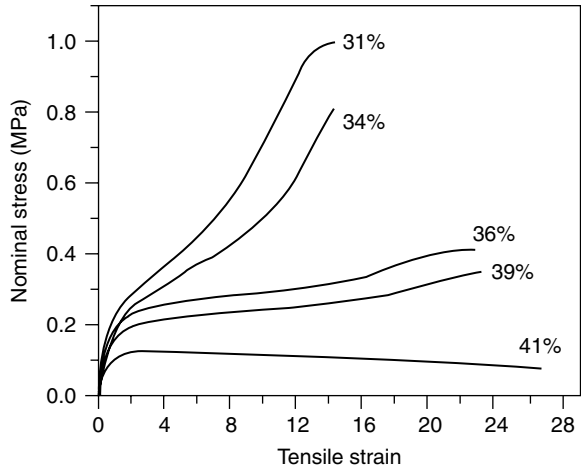


FIGURE 7.35 Tensile stress–strain curves to break of PVP–PEG blends, containing 31, 34, 36, 39, and 41 wt % PEG-400 at 8–9% degree of hydration. Drawing rate is 20 mm/min. (From Novikov, M.B., Roos, A., Creton, C., and Feldstein, M.M., *Polymer*, 44(12), 3559, 2003. With permission.)

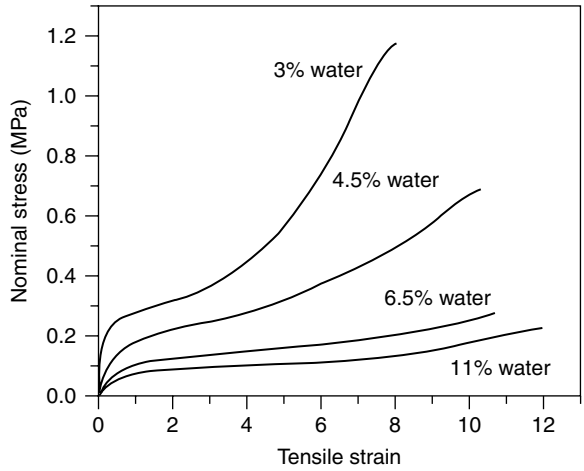


FIGURE 7.36 Impact of water content in PVP blends with 36 wt % PEG-400 on tensile stress–strain curves to deform and break the PVP–PEG complex under uniaxial drawing with a rate of 20 mm/min. (From Novikov, M.B., Roos, A., Creton, C., and Feldstein, M.M., *Polymer*, 44(12), 3559, 2003. With permission.)

water, results in increased elongation at break, ε_b. Let us recall that the ε_b quantity is an indirect measure of free volume.[27] However, with the increase in PEG concentration the value of ε_b increases linearly (Figure 7.37), whereas the same plot for the effect of water reveals a faster growth of ε_b in dry blends than in hydrated compositions (Figure 7.38). For PVP blends containing less than 36% PEG, the ultimate tensile strength, σ_b, is

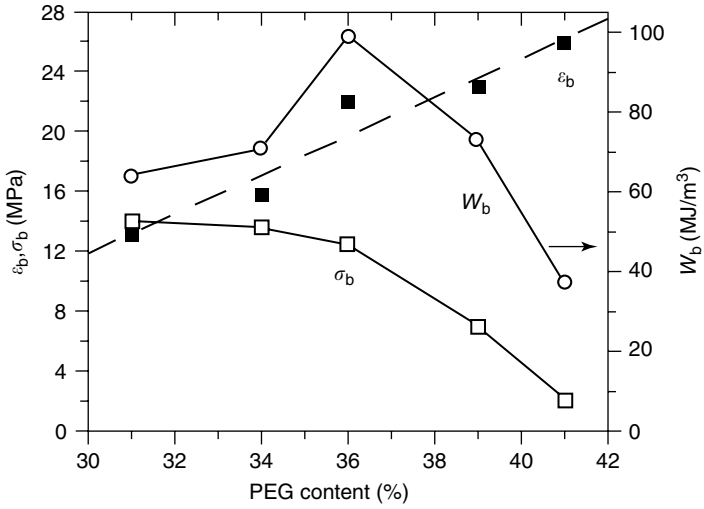


FIGURE 7.37 The total work of viscoelastic deformation to break the PVP–PEG film, W_b, the ultimate tensile strength, σ_b, and the break elongation, ε_b, as a function of PEG concentration in blends. The extension rate is 20 mm/min. (From Novikov, M.B., Roos, A., Creton, C., and Feldstein, M.M., *Polymer*, 44(12), 3559, 2003. With permission.)

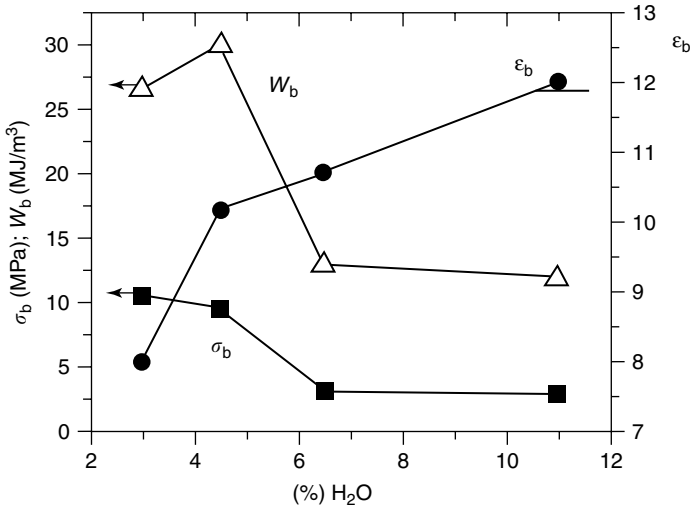


FIGURE 7.38 Effect of water content in PVP–PEG (36%) adhesive hydrogel on the total work of viscoelastic deformation to break the PVP–PEG film, W_b, the ultimate tensile strength, σ_b, and the break elongation, ε_b. Drawing rate is 20 mm/min. (From Novikov, M.B., Roos, A., Creton, C., and Feldstein, M.M., *Polymer*, 44(12), 3559, 2003. With permission.)

comparatively high and practically unaffected by PEG content. It should be pointed out that the σ_b quantity is a measure of the cohesive strength of the deformed polymer.[27] In contrast, at PEG concentrations higher than 36% the σ_b value declines rapidly with PEG amount (Figure 7.37). At the same time, absorbed water smoothly decreases the cohesive strength of the blends, expressed in terms of σ_b quantity (Figure 7.38). In this way, although PEG induces a plasticization of glassy PVP, it couples the properties of plasticizer at small strains and an enhancer of cohesive strength at large strains, which dominate within different composition regions. At PEG content below the composition of the PVP–PEG blend that provides the best adhesion (36 wt %),[27] the rise in PEG concentration enhances both the cohesive toughness (ultimate strength to break) and the ductility (break elongation) of the adhesive polymer, indicating that PVP cross-linking through H-bonding via terminal hydroxyl groups at PEG short chains is accompanied also by a plasticization effect.

At PEG concentrations higher than 36 wt %, the PEG behaves only as a plasticizer, decreasing the cohesive toughness and increasing maximum elongation at fracture. The behavior of water in the PVP–PEG hydrogels, on the other hand, has a typical plasticizing effect, decreasing the elasticity modulus, E, but leaving the large strain behavior unchanged. The value of the total work of viscoelastic deformation to break the PVP–PEG adhesive hydrogels, W_b, tends to decrease with water content, especially at hydration levels higher than 5% (Figure 7.38). In contrast, the dependence of the total work of viscoelastic deformation to break the PVP–PEG film, W_b, on PEG content (Figure 7.37) correlates well with both peel and probe tack adhesion[27] and reveals a maximum at 36% PEG concentration for the blend demonstrating the best adhesion.

Thus, the effect of CLC on cohesive toughness and ductility of plasticized FFP is completely opposite the effect of LLC. Whereas the addition of LLC causes enhanced cohesion and decreased free volume (ductility), the CLC increases cohesion to a lesser extent and couples this effect with behavior typical of a plasticizer (increased free volume and deformability). However, it is pertinent to note that low-molecular-weight PEG is a liquid with a glass transition temperature typical of a plasticizer, about −70°C. Therefore, it remains to be seen whether such behavior is typical of CLCs with higher T_g values.

7.4.3 Adhesive Properties

To appreciate the significance of the T_g value for the behaviors of various CLCs, we compare the adhesive properties of the PVP–PEG system with those observed for the blends of other FFP and CLC.

7.4.3.1 Poly(Vinyl Pyrrolidone)—Poly(Ethylene Glycol) Complexes

Adhesion of PVP–PEG blends has been studied with peel[142] and probe tack[141] tests and is reviewed briefly in *Fundamentals of Pressure Sensitivity*, Chapter 10.[27] In the following sections we therefore focus on probe tack data, which are in good agreement with peel results.

In the probe tack test, a high value of maximum stress and a sharp peak of stress signify a brittle-like behavior of material and adhesive type of debonding without elongational

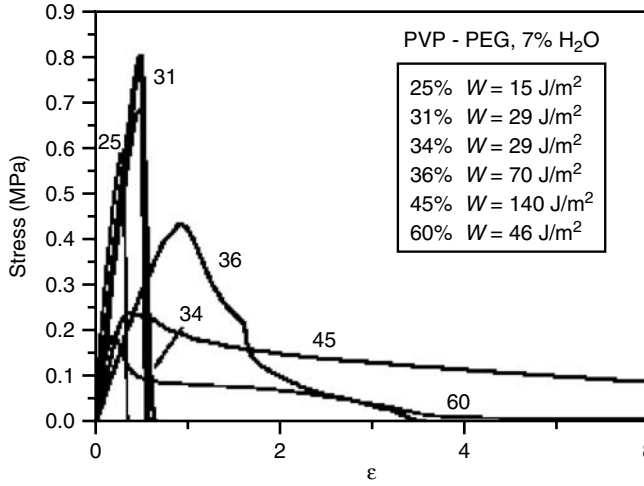


FIGURE 7.39 Probe tack stress–strain curves for the blends of high-molecular-weight PVP with different amounts of PEG-400 under a debonding rate of 0.1 mm/s. The contents of PEG-400 are indicated.

flow and fibrillation (see *Fundamentals of Pressure Sensitivity*, Chapter 6). As follows from the probe tack curves illustrated in Figure 7.39, this type of curve is a characteristic feature of PEG underloaded blends (up to 34 wt % PEG). Above this threshold the blends gain ductility. As a result, the stress peak shifts toward higher elongations (36% PEG) and the maximum stress drops. The decrease in maximum stress with plasticization implies that less energy is required to induce the cavitation of adhesive material (or that large defects are present at the interface due to the higher modulus of the material). A particular feature of the PVP–PEG adhesive is an abrupt transition from an adhesive type of debonding to a miscellaneous mechanism that is inherent to the 36% PEG blend. The occurrence of a plateau on stress–strain curves for the blends overloaded with PEG is evidence in favor of fibrillation. The value of the plateau stress characterizes the strength of fibrils, which increases with decreased PEG content. The value of practical work of adhesion, W, defined as the area under the probe tack curve, goes through a maximum at 45% concentration of PEG-400, implying that the fibrillation process is a major energy-dissipating mechanism for PSAs. A PVP blend with 45% PEG is too fluid and demonstrates a cohesive type of debonding. Among the other blends, the highest value of the work of debonding demonstrates the blend containing 36% PEG, which also exhibits the best peel adhesion.[27,142]

The effect of the CLC, PEG, on probe tack of PVP–PEG blends is in evident contrast with that of the LLC in Eudragit E-100 blends with Eudragit L-100-55 (compare Figures 7.39 and 7.19). The impact of PEG-400 on probe tack adhesion is more typical of the effect of plasticizer (TEC) in the ladder-like Eudragit E-100 complex with Eudragit L-100-55 than of the cross-linker (see Figure 7.20). Whereas the increase in the content of the LLC (Eudragit L-100-55) causes a loss of adhesion (Figure 7.19), the CLC, PEG, improves adhesion (Figure 7.39).

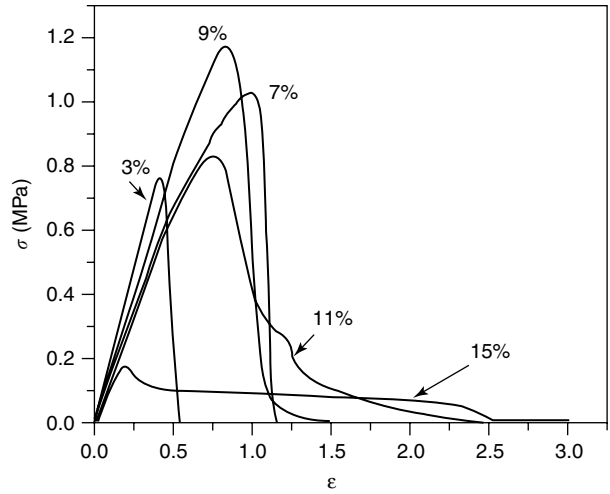


FIGURE 7.40 Effect of absorbed water on probe tack of PVP–PEG binary blends, containing 36 wt % PEG-400. (From Cleary, G.W., Singh, P., and Feldstein, M.M., Proceedings of the 28th Annual Meeting of the Adhesion Society, Mobile, AL, 460, 2005. With permission.)

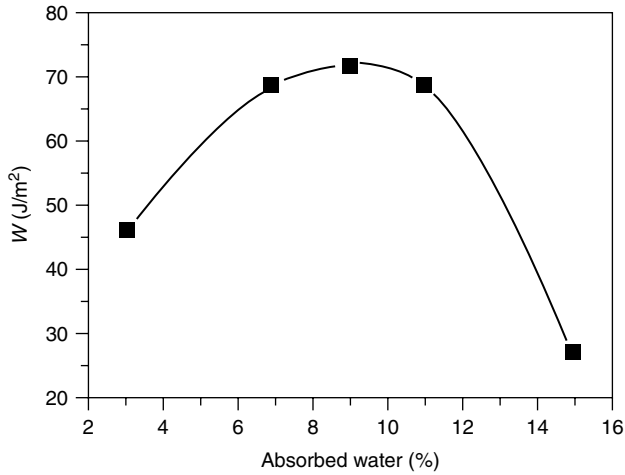


FIGURE 7.41 The work of adhesive debonding as a function of the content of absorbed water in PVP–PEG blends. (From Cleary, G.W., Singh, P., and Feldstein, M.M., Proceedings of the 28th Annual Meeting of the Adhesion Society, Mobile, AL, 460, 2005. With permission.)

Whereas PEG combines the effects of hydrogen bonding cross-linker and plasticizer, water behaves only as the plasticizer of glassy PVP. Concentrated aqueous solutions of high-molecular-weight PVP are too cohesively weak to be employed as PSAs. The adhesion of PVP–PEG blends increases with blend hydration, going through a maximum at 9% water (Figures 7.40[143] and 7.41). The blends containing up to 7% water

behave as solid materials and a fibrillation plateau appears in the probe tack curves at 9% water concentration. A further increase in blend hydration leads to a continuous plateau, implying that absorbed water plays an important role in the PSA behavior of PVP–PEG blends. Thus, PVP–PEG blends can be regarded as hydroactivated adhesives. This behavior is absolutely atypical of conventional hydrophobic PSAs and makes hydrophilic PVP–PEG adhesives perform like typical bioadhesives; thus, it is useful for applications to highly hydrated biological substrates such as teeth and mucosal membranes.

7.4.3.2 Polyelecrolyte Complexes

A typical example of CLC with high T_g is succinic (butanedioic) acid (SA, HOOC—$(CH_2)_2$—COOH), which has been reported to form strong complexes with polybases such as Eudragit E-100.[49] A PSA based on polybase Eudragit E-100 blends with SA is known as the Plastoid® E 35 adhesive and is commercially available from Röhm Pharma Darmstadt (Germany). Because SA is a crystalline substance with T_m = 188–190°C and T_g = 88°C, preparation of the PSA comprising the Eudragit E-100 blend with SA requires the use of plasticizers such as TEC.

As illustrated by the probe tack curves in Figure 7.42, the effect of CLC (SA) on adhesion is similar to that of LLC (Eudragit L-100-55) for blends containing the same FFP, Eudragit E-100, as a polybase. Comparison of Figures 7.42 and 7.19 demonstrates that the addition of SA to Eudragit E-100 results in increased peak stress value and decreased maximum elongation and, as a consequence, leads to a reduction in detaching energy. Nevertheless, depression of the plateau on the probe tack curves (which relates

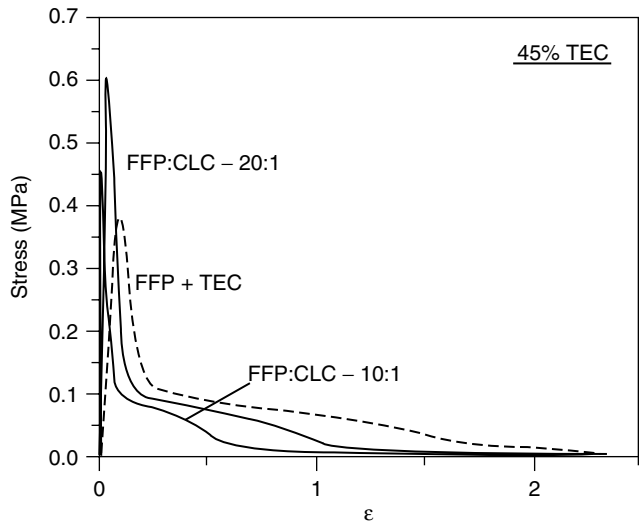


FIGURE 7.42 Effect of succinic acid (CLC) on the adhesive properties of Eudragit E-100 carcass-like complex. The concentration of the plasticizer (TEC) is 45%.

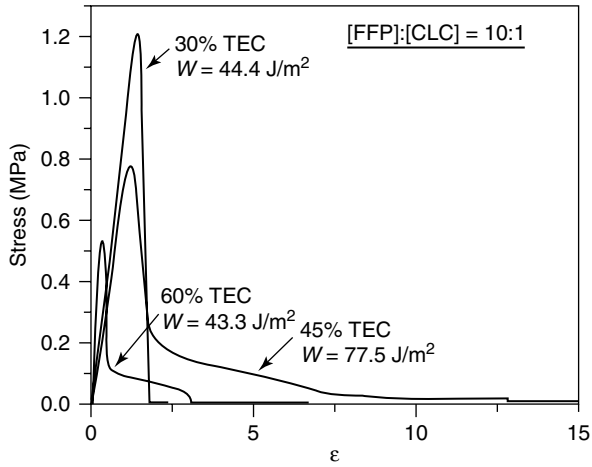


FIGURE 7.43 Effect of plasticizer concentration (TEC) on probe tack behavior of the carcass-like complex between Eudragit E-100 (FFP) and succinic acid (CLC). FFP:CLC = 10:1.

to inhibition of the fibrillation process) is significantly less pronounced in the case of short-chain CLC, SA, than for long-chain LLC, Eudragit L-100-55. Thus, the enhancement of cohesion due to the gain in free volume is a common property of both CLC and LLC. Coupling of FFP cross-linking with plasticization and tack improvement is a unique feature of short-chain PEG and other low T_g telechelics.

The effect of plasticizer, TEC, on the adhesive properties of CLC Eudragit E-100 with SA is illustrated in Figure 7.43. Comparison of these data with the probe tack curves in Figure 7.20 for the ladder-like Eudragit E-100 complex with Eudragit L-100-55 demonstrates that the effect of FFP plasticization on adhesion is qualitatively similar for the ladder-like and carcass-like interpolymer complexes. In the same manner as for the Eudragit E-100–Eudragit L-100-55 system, with the rise in plasticizer concentration the adhesion of Eudragit E-100 blends with SA goes through a maximum at 45% TEC content. However, both maximum stress and the work of debonding for CLCs of Eudragit E-100 with SA are appreciably greater than those for the LLC of the same FFP with Eudragit L-100-55.

7.4.4 Water Absorption and Dissolution in Water

Taking into account that carcass-like network junctions represent single hydrogen or electrostatic bonds but not the sequences of greater numbers of bonds, as in the case of LLCs, we can expect the CLCs to be relatively more soluble than their ladder-like counterparts. This was observed experimentally when the LLC formation between water-soluble polymers resulted in loss/reduction of solubility, whereas the CLC was soluble. The Corplex adhesives based on CLCs with tailored performance properties are available from Corium International, Inc.[144]

7.5 Adhesives Combining the Ladder-Like and Carcass-Like Types of Noncovalent Cross-Linking

7.5.1 Competitive Hydrogen Bonding and the Role of Absorbed Water in the Blends of Film-Forming Polymer with Carcass-Like and Ladder-Like Cross-Linkers

In contrast to the hydrophobic PSAs, the adhesion of PVP–PEG blends increases appreciably with moisture. However, practical applicability of PVP–PEG PSAs in hydrated environments is essentially limited by the fast dissolution of the PVP–PEG complex in water. The interpolymer complexes of hydrophilic water-soluble polymers formed via hydrogen or electrostatic bonding between complementary functional groups located in the repeating units of both polymer backbones behave as hydrogels, which are water-swellable but insoluble in water.[145] It is reasonable to use the ladder-like type of interpolymer complex to render the PVP–PEG hydrophilic PSA insoluble in water. The LLC can be incorporated into the PVP–PEG blend (e.g., the copolymer of MAA with EA, Eudragit L-100-55) (Table 7.1). The scheme of the structure of the interpolymer complex among an FFP, a CLC, and an LLC is presented in Figure 7.44.

The carboxyl groups in the Eudragit L-100-55 copolymer are capable of forming an LLC with the carbonyls in repeating units of long-chain PVP and with oxygen atoms of oxyethylene units in PEG short chains.[146] Terminal hydroxyl groups of PEG form hydrogen bonds both to the carbonyl groups in the PVP repeat units and to the carboxyl groups of Eudragit L-100-55 and cause PEG self-association through hydrogen bonding to other PEG hydroxyl groups and oxygen atoms in the PEG oxyethylene units. Each of these types of hydrogen bonding leads to the formation of CLCs. PEG self-associates and complexes with Eudragit L-100-55 are not illustrated in Figure 7.44 for the sake of simplicity. In addition, the ternary PVP–PEG-LLC blends contain molecules of absorbed water, which participate in H-bonding.

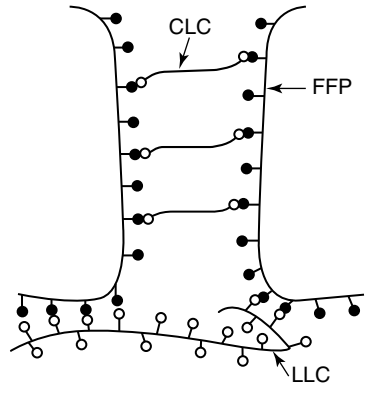


FIGURE 7.44 Schematic view of the interpolymer complex based on a combination of the carcass-like and ladder-like types of interpolymer complexes. FFP is a film-forming polymer, CCL is a carcass-like cross-linker, and LLC is a ladder-like cross-linker.

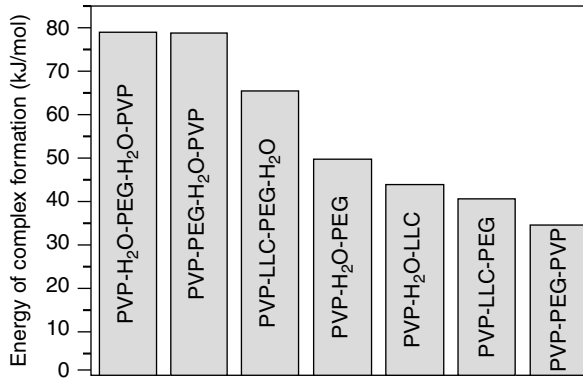


FIGURE 7.45 Most strong types of hydrogen bonding in PVP–PEG–Eudragit L-100-55 blends containing water absorbed from the atmosphere.

To evaluate the relative strengths of hydrogen-bonded complexes in PVP–PEG–Eudragit L-100-55 blends, FTIR spectroscopy investigations and quantum-chemical calculations were performed.[146] According to this analysis, the energy of H-bonding diminished in the order PVP–LLC–PEG(OH) > PVP–(OH)PEG(OH)–PVP > PVP–H_2O > PVP–PEG(OH) > LLC–PEG(–O–) > PVP–LLC > LLC–PEG(OH). Thus, most stable complexes are the triple PVP–LLC–PEG(OH) complex and the complex wherein comparatively short PEG chains simultaneously form two hydrogen bonds to PVP carbonyl groups through both terminal OH-groups, acting as H-bonding cross-links between longer PVP backbones. Incorporation of water molecules into the hydrogen bonding of complementary functional groups of polymer components is capable of significantly increasing the strength of formed interpolymer complexes. As a result, the most energetically favorable complex in the PVP–PEG–Eudragit L-100-55–H_2O system is a network structure formed due to hydrogen bonding of both PEG terminal hydroxyl groups to the carbonyl groups in PVP monomer units through two water molecules located between the reactive functional groups of the polymers (PVP–H_2O–PEG–H_2O–PVP; Figure 7.45). EA monomer units of Eudragit L-100-55 do not contribute appreciably to interpolymer hydrogen bonding.

7.5.2 Phase State of Poly(Vinyl Pyrrolidone)–Poly(Ethylene Glycol)–Ladder-Like Cross-Linker Blends

7.5.2.1 Effect of Ladder-Like Cross-Linker

Competitive hydrogen bonding governs the phase state of triple polymer blends. We consider first the effect of LLC, Eudragit L-100-55, on the phase state of the PVP–PEG system. It is pertinent to note once more that the binary PVP–PEG system is a single phase and involves reversible cross-linking of PVP macromolecules via hydrogen bonding through the terminal OH groups of short-chain PEG. As follows from the data in Figure 7.46,[146] blends containing less than 30 wt % Eudragit L-100-55 possess a single glass transition and are miscible. However, the PVP–PEG blend with 35.7% Eudragit

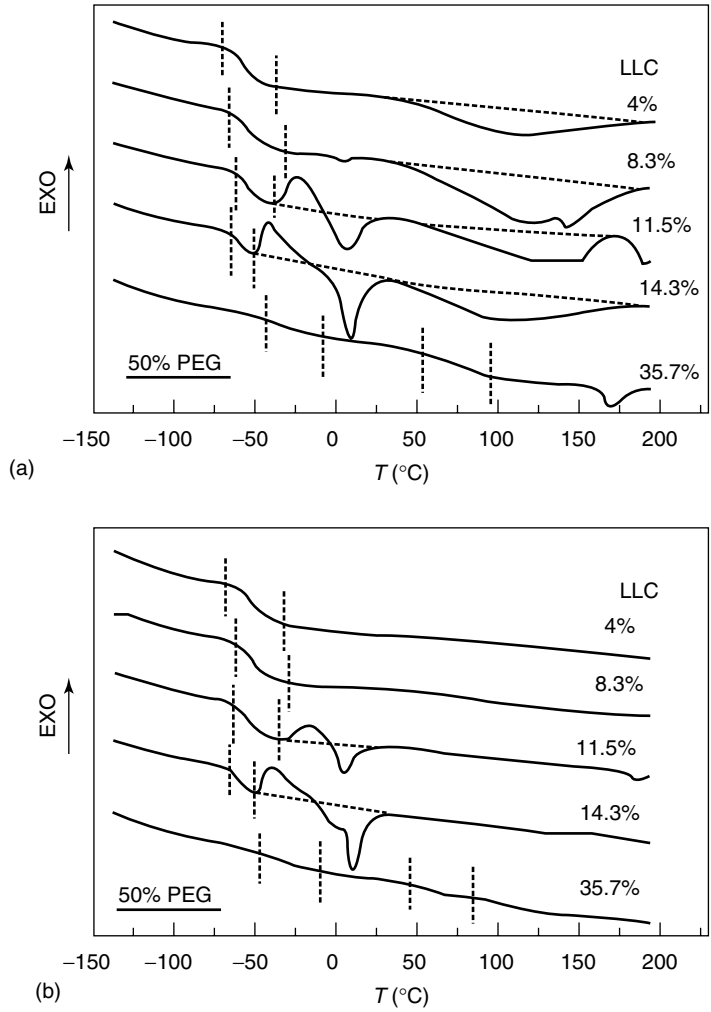


FIGURE 7.46 DSC heating thermograms of ternary PVP–PEG–Eudragit L-100-55 blends containing different amounts of LLC (Eudragit L-100-55) and 50 wt % PEG-400. A, Hydrated blends containing 3 wt % absorbed water; B, dry blends. (From Kireeva, P.E., Shandryuk, G.A., Kostina, J.V., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Appl. Polym. Sci.,* 105(5), 3017, 2007. With permission.)

L-100-55 demonstrates two T_g's of −38 and 55°C. Both T_g values are atypical of parent components and are composition dependent, implying that they relate to mixed phases and that the system is partially compatible. Based on the results of phase state investigation of binary PVP–PEG blends,[126,131] the lower-T_g phase can be logically related to the PVP–PEG–Eudragit L-100-55 complex, whereas the upper-T_g phase corresponds most likely to the phase enriched with Eudragit L-100-55. Further increase in the Eudragit L-100-55 concentration leads to rapid growth of the upper-T_g value.

The most surprising feature of the DSC traces illustrated in Figure 7.46 is that the endotherm of PEG melting coupled with its symmetric exotherm of PEG cold crystallization appears in the range between 10 and 30 wt % Eudragit L-100-55 and vanishes as its amount becomes as high as 36%. In blends containing less than 9 wt % Eudragit L-100-55, all PEG is associated with PVP in the amorphous phase and is unavailable for crystallization. This fact is readily explained because in binary PVP blends with PEG-400 the crystalline phase arises as the PEG content achieves 45–50 wt %.[126,131]

Thus, the analysis of PEG melting endotherms in DSC traces of ternary PVP–PEG–Eudragit L-100-55 blends provides information about the state of CLC (PEG) in the blends. The increase in LLC content leads to the appearance of crystallizable (unbound) PEG due to the partial replacement of PEG in the PVP–PEG complex by the LLC (Eudragit L-100-55). Based on this observation we are able to conclude that the carboxyl groups of Eudragit L-100-55 form stronger hydrogen bonds with PVP carbonyls than with PEG-400. This conclusion is confirmed by the data of quantum chemical calculations presented above. At higher LLC concentrations, all PEG becomes associated with Eudragit L-100-55. This allows us to characterize the PVP–PEG–Eudragit L-100-55 blends as a system with strong favorable and competing interactions between components of the blend.

7.5.2.2 Effect of Carcass-Like Cross-Linker

The effect of PEG content on DSC curves of triple PVP–Eudragit L-100-55–PEG blends is illustrated in Figure 7.47.[146] The ratio between the FFP (PVP) and LLC (Eudragit L-100-55) concentrations is fixed at 5:1. With the rise of PEG content, T_g decreases smoothly, as illustrated in Figure 7.47. This finding implies that PEG-400 acts as a good plasticizer for the PVP–Eudragit L-100-55 LLC.

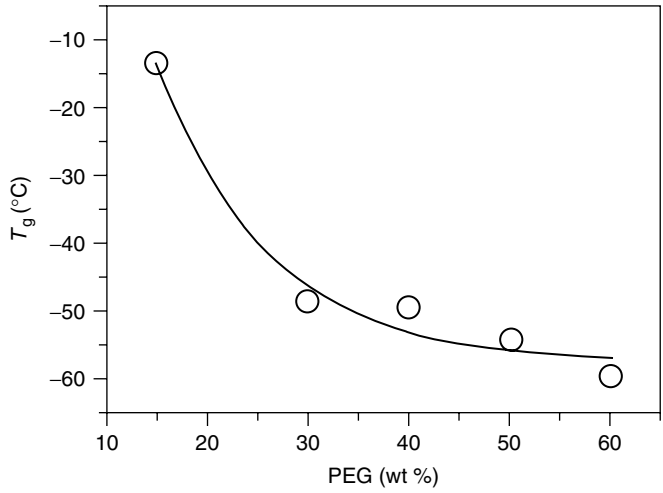


FIGURE 7.47 Relationship of glass transition temperature to the concentration of PEG-400 in PVP–PEG–Eudragit L-100-55 blends. [PVP]:[Eudragit L-100-55] = 5:1. (From Kireeva, P.E., Shandryuk, G.A., Kostina, J.V., Bondarenko, G.N., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Appl. Polym. Sci.,* 105(5), 3017, 2007. With permission.)

7.5.3 Mechanical Properties

7.5.3.1 Impact of Ladder-Like Cross-Linker Concentration

The effect of LLC (Eudragit L-100-55) concentration on the tensile properties of ternary PVP–PEG–LLC blends containing 50% PEG-400 is illustrated in Figure 7.48.[147] The shape of the stress–strain curves changes significantly with the increase in LLC content. The increase in LLC concentration causes an appreciable gain in mechanical strength (ultimate tensile stress at break, σ_b) and loss of compliance, manifested by the decrease in maximum elongation, ε_b. The mechanical behavior of binary PVP–PEG blend is similar to that for the ternary PVP–PEG–Eudragit L-100-55 system containing 4 wt % LLC. Whereas the blends containing 6 and 8% LLC reveal a deformation mechanism typical of rubbers, the blend with 12% LLC demonstrates behavior typical of cured elastomers. The tensile modulus, *E*, may be determined as the slope of the initial linear region of the stress–strain curve, where Hooke's law is applicable and considered a material constant, characterizing polymer elasticity. As illustrated in Figure 7.49, with the rise in LLC concentration the modulus increases significantly. This fact indicates a sharp increase in ladder-like network density.

The value of ultimate tensile stress at break of the stretched film is an integral measure of the cohesive strength of the strained material. At the same time, as demonstrated for binary PVP–PEG blends, the larger the free volume, the higher the value of maximum elongation at the point of break (see *Fundamentals of Pressure Sensitivity*, Chapter 10).[27] As demonstrated previously (see Section 7.4.2), formation of the CLC PVP–PEG complex leads to enhanced cohesive strength and large free volume (which determines the

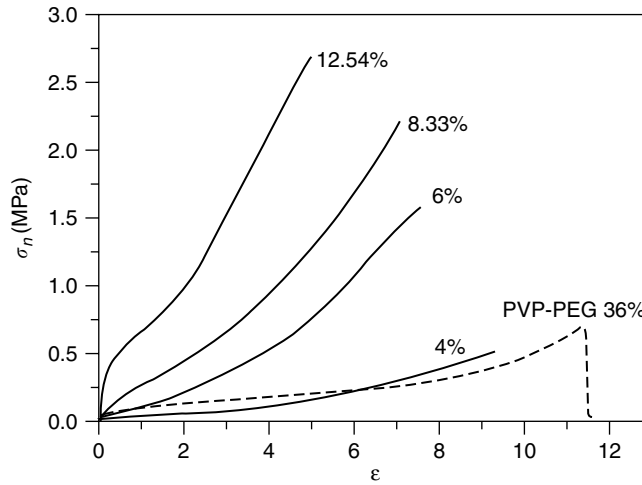


FIGURE 7.48 Stress–strain curves for ternary PVP–PEG–LLC blends containing 50% PEG and constant content of absorbed water (7 wt %) obtained under uniaxial drawing with the rate of 1 mm/s. The dashed curve relates to the PVP–PEG binary blend containing 36 wt % PEG-400. The contents of LLC are indicated. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

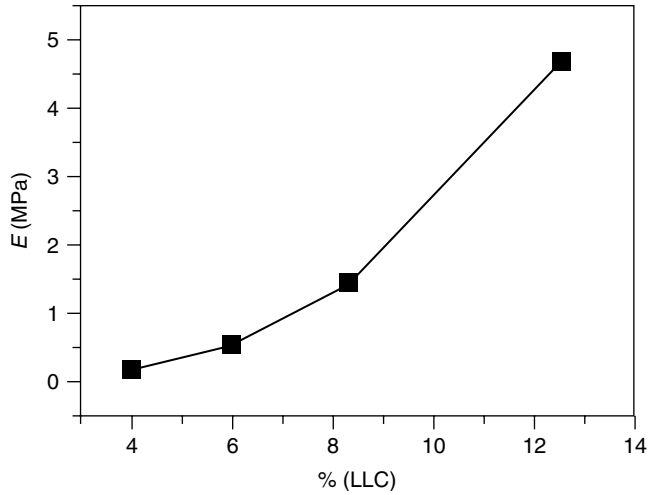


FIGURE 7.49 Effect of LLC content on the tensile modulus of ternary PVP–PEG–Eudragit L-100-55 blends containing 50% PEG. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

adhesive properties of PVP–PEG blends). In contrast to this behavior, the formation of the LLC is accompanied by increased cohesive strength, coupled with a decrease in free volume.

7.5.3.2 Effect of Poly(Ethylene Glycol) Content on Tensile Stress–Strain Curves

We consider now the effect of CLC (PEG) concentration on tensile deformation of ternary PVP–PEG–Eudragit L-100-55 blends (Figure 7.50). The blend containing 30% PEG deforms as a tough, solid material, exhibiting a pronounced effect of strain hardening, whereas the blend with 60% PEG reveals comparatively much more expressed liquid-like behavior. The CLC, PEG, is a good plasticizer for PVP blends with the LLC, Eudragit L-100-55. As evident from the data illustrated in Figure 7.50, the rise in PEG content promotes the ductility of PVP–PEG–LLC blends by increasing the free volume.

The data in Figure 7.51 indicate a principal difference in the effects of LLC (Eudragit® L-100-55) and CLC (PEG-400) on tensile deformation of ternary PVP–PEG–Eudragit L-100-55 blends.[147] It should be remembered that the values of ultimate tensile stress (σ_b) and maximum elongation (ε_b) at break of the stretched polymer film are, respectively, indirect characteristics of cohesive strength and free volume of the strained polymer, whereas the work of viscoelastic deformation up to the break of the polymer film, W_b, characterizes the amount of energy required to stretch and break the polymer film. As evident from the data illustrated in Figure 7.51, the LLC (Eudragit L-100-55) increases appreciably the cohesive strength (σ_b) and decreases the free volume (ε_b), acting like an interpolymer covalent cross-linker. Whereas the maximum elongation is a monotonously decreasing function of LLC content, tensile strength, σ_b, goes through a maximum at 8% LLC concentration and then demonstrates negligible reduction. At the same

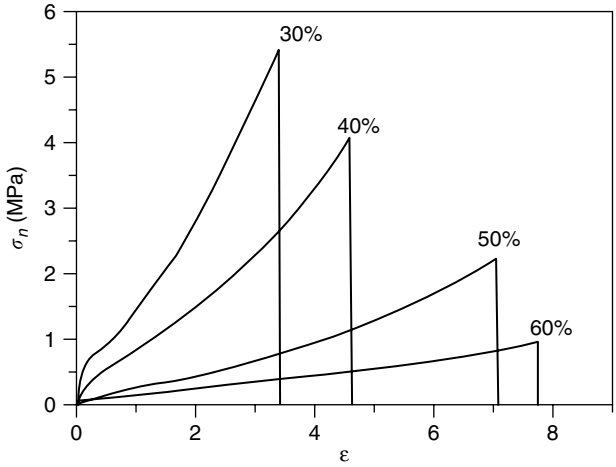


FIGURE 7.50 Impact of CLC (PEG) concentration on the deformation of PVP–PEG–LLC blends. The PVP:LLC ratio is 5:1. The content of absorbed water is 7%. Tensile rate is 1 mm/s. PEG concentrations are indicated.

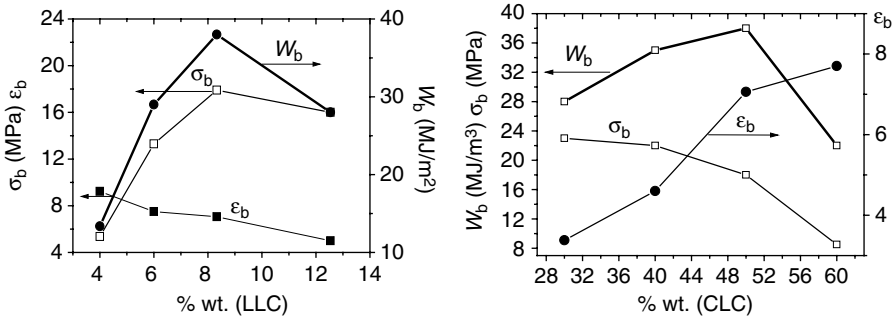


FIGURE 7.51 Effects of LLC (left) and CLC (right) content on total work to deform and break the PVP–PEG–LLC adhesive film, W_b, ultimate tensile strength, σ_b, and break elongation, ε_b. Tensile rate is 1 mm/s. Content of absorbed water is 7 wt %. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

time, the CLC (PEG-400) causes a smooth decrease in σ_b and appreciable increase in ε_b, serving as a typical plasticizer of the PVP–PEG–Eudragit L-100-55 system. The role of PEG as cross-linker is thus diminished in the triple blends in contrast to the binary PVP–PEG blends.

7.5.3.3 Influence of Extension Rate

As demonstrated previously for binary PVP–PEG adhesive blends, a particular feature of the hydrogen-bonded PVP–PEG network is the existence of a well-defined time for its structural rearrangement, which, in turn, depends upon the life time of H-bonded network

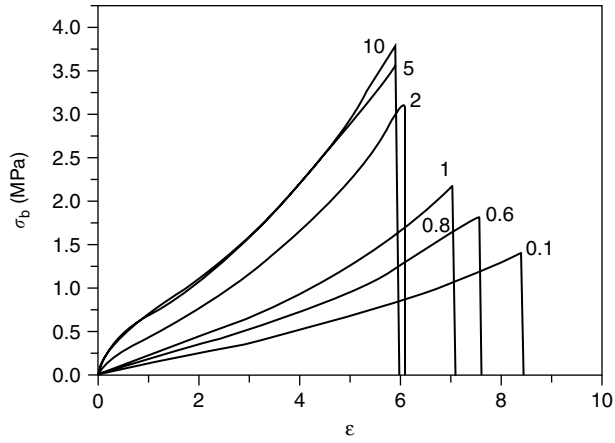


FIGURE 7.52 Effect of tensile rate on the stress–strain curves of PVP–PEG–LLC blends containing 50% PEG, 8.33% LLC, and 7 wt % absorbed water. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

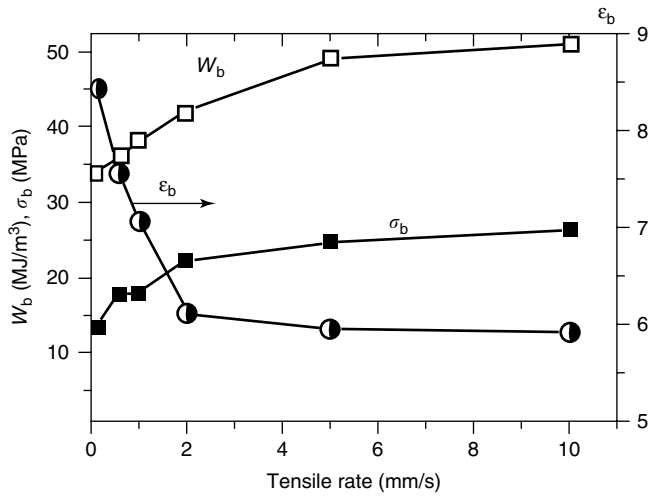


FIGURE 7.53 Impact of tensile rate upon the mechanical properties of PVP–PEG–LLC blends. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

junctions under applied mechanical stress. Figures 7.52 and 7.53 demonstrate the effect of tensile rate on the mechanism of deformation of ternary PVP–PEG–Eudragit L-100-55 blends.[147] The shape of the stress–strain curves for the ternary blends is similar to that of cured elastomers, with a pronounced plateau and stress-hardening effect. With the increase in tensile rates from 0.1 to 10 mm/s, the curve shape and the mechanism of debonding remain the same. This is due to the nature of the mechanism of the interaction in the LLC.

Formation of the LLC interpolymer complex, in addition to the carcass-like PVP–PEG complex, slows down the relaxation processes in such ternary blends. Both the relaxation time and the life time of the ladder-like network junction in the ternary blend are appreciably longer that those of the carcass-like junction in the binary PVP–PEG system. With the increased tensile rate, the tensile strength (σ_b) and the value of the total work of debonding, W_b, grow smoothly, tending to the limiting values at drawing rates higher than 2 mm/s (Figure 7.53). The value of ultimate elongation (ε_b) sharply drops in the range of tensile rates between 0.1 and 2 mm/s and remains practically constant at higher debonding rates.

7.5.4 Adhesive Behavior

7.5.4.1 Effect of Ladder-Like Cross-Linker

The significance of the data presented in Figure 7.51 is that the LLC increases the energy of cohesive interaction and decreases appreciably the free volume in ternary PVP–PEG–Eudragit L-100-55 blends. Because the ratio between cohesive strength and free volume is a factor that accounts for the adhesive ability of the material, and taking into consideration that the carcass-like PVP–PEG complex is tacky, it is logical to expect that adding the LLC (Eudragit L-100-55) to the carcass-like PVP–PEG complex would upset the specific balance between cohesion and free volume and deteriorate adhesion. The probe tack curves presented in Figures 7.54 and 7.55 demonstrate that incorporation of the LLC (Eudragit L-100-55) into binary PVP–PEG adhesive blends has negligible effect on the value of maximum stress, but essentially decreases the work of debonding (area under the stress–strain curve).[147]

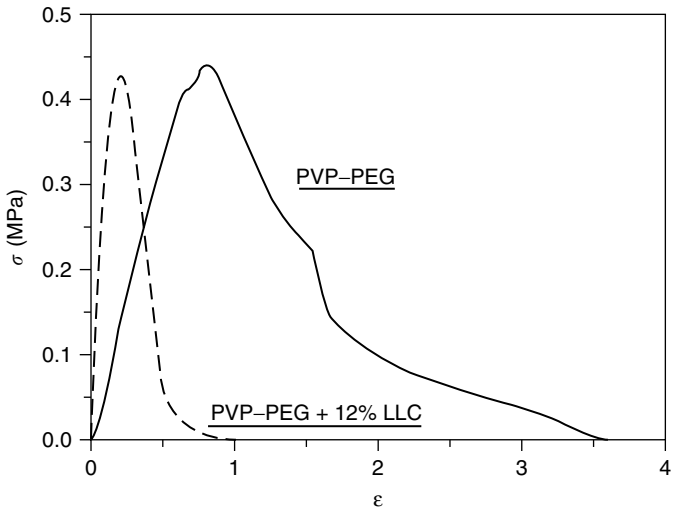


FIGURE 7.54 Probe tack curves of binary PVP–PEG (36 wt %) and ternary PVP–PEG (29%)–LLC (Eudragit L-100-55, 12%) blends. The debonding rate is 0.1 mm/s. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

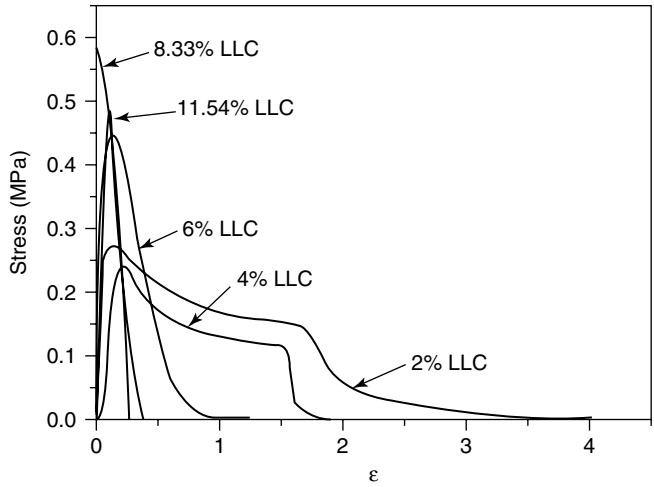


FIGURE 7.55 Effect of LLC concentration (Eudragit L-100-55) on probe tack stress–strain curves of PVP–PEG (50 wt %)–LLC triple blends. The content of absorbed water is 7 wt %. The debonding rate is 0.1 mm/s. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol*., 21(7), 531, 2007. With permission.)

The transition from a liquid–like mechanism of deformation to a solid–like mechanism with increased LLC concentration is illustrated in Figure 7.55.[147] The blend containing 2 wt % Eudragit L-100-55 deforms as a typical PSA. Twofold increase in the LLC content leads to the rapid reduction of free volume and, as a consequence, to a decrease in maximum elongation. Further increase in LLC concentration results in growth of the cohesive strength and cavitation stress, which achieves a maximum at 8 wt % Eudragit L-100-55 blends. If the LLC concentration increases further, the maximum stress begins to decrease because the material under this debonding rate becomes brittle-like. The practical work of adhesion, W, is the decreasing function of the Eudragit L-100-55 concentration that achieves its limiting value ($W = 37$ J/m^2) at 4% LLC.[147]

7.5.4.2 Effects of Cross-Linking Polymer Nature and Interpolymer Bonding Type

Eudragit L-100-55 is not a unique carboxyl-containing polymer that can be employed as an LLC for FFPs (PVP). Figure 7.56 illustrates the effect of another polyacid, hydroxypropylmethylcellulose phthalate (HPMCP). With the rise in LLC concentration, the transition toward solid-like behavior without adhesive material fibrillation is observed for the HPMCP-containing system. The HPMCP is a much more rigid-chain polymer than Eudragit L-100-55. In the PVP–PEG–HPMCP complex both the maximum stress and the work of debonding go through a maximum at 15% LLC concentration.

Owing to the presence of carboxyl groups, Eudragit L-100-55 is a pH-sensitive polymer. With the rise in pH value, neutralization occurs, which makes its carboxyl groups

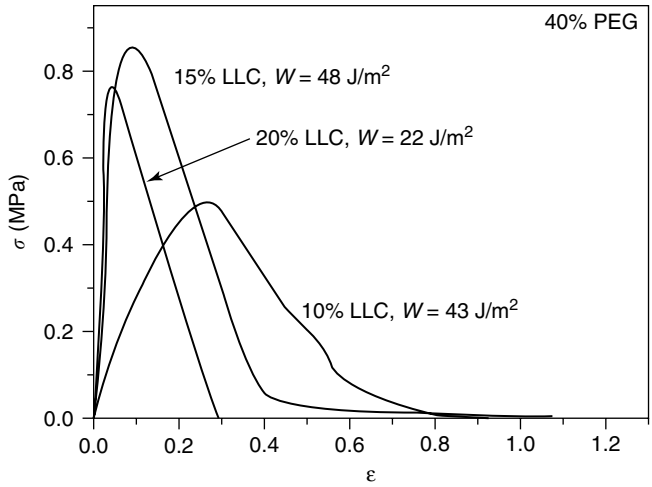


FIGURE 7.56 Effect of LLC concentration (hydroxypropylmethylcellulose phthalate, HPMCP) on tack of PVP–PEG–LLC blends. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

partially ionized. The effect of LLC ionization by treatment of the polyacid with NaOH solution will impact adhesion for the following reasons.

1. Only nonionized carboxyl groups are capable of forming H-bonds with complementary groups in PVP and PEG. This factor affects mainly the network density of H-bonds and cohesive strength.
2. As a result of electrostatic repulsion between carboxylate anions, the LLC chains become extended and free volume increases.

The probe tack data in Figure 7.57 demonstrate that partial ionization of the ionogenic groups in Eudragit L-100-55 results in tack improvement, but does not change the mechanism of debonding that remains solid-like and is not accompanied by fibrillation for the PVP–PEG–LLC blend.

7.5.4.3 Impact of Carcass-Like Cross-Linker Concentration in Blends

Figure 7.58 demonstrates the effect of CLC (PEG-400) on tack in PVP–PEG–Eudragit L-100-55 blends.[147] As in binary PVP–PEG blends (Figure 7.39), CLC (PEG) acts as a plasticizer in the PVP–PEG–LLC ternary system by promoting the fibrillation process and increasing the value of maximum elongation. In this respect, the effect of the increase in PEG concentration is similar to the decrease in LLC content (Figures 7.54 and 7.55). As demonstrated by comparison of the curves in Figure 7.58, the value of practical work of adhesion (W) grows monotonously with the increase in PEG concentration up to 60%, implying that PEG is an enhancer of adhesion of PVP–PEG–Eudragit L-100-55 blends, whereas the peak stress goes through a maximum at 40% PEG-400 in blends. The value of the maximum force to debond the probe from the surface of substrate is traditionally

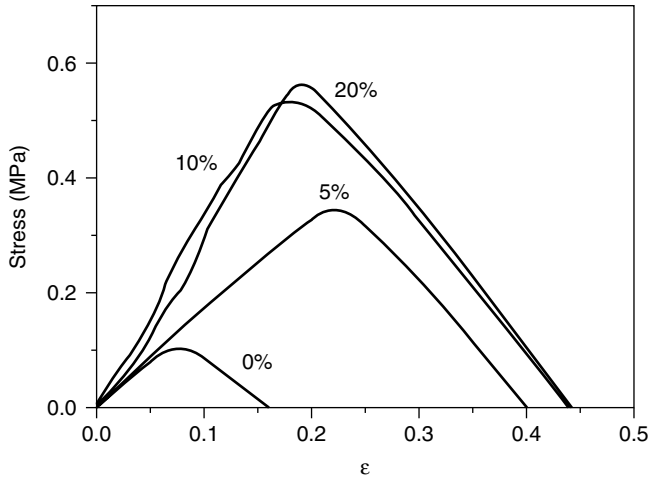


FIGURE 7.57 Impact of ionization of carboxyl groups of LLC (Eudragit L-100-55) upon the stress–strain curves of the PVP–PEG–LLC adhesive system containing 12 wt % absorbed water. The degrees of ionization (%) are illustrated. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol*., 21(7), 531, 2007. With permission.)

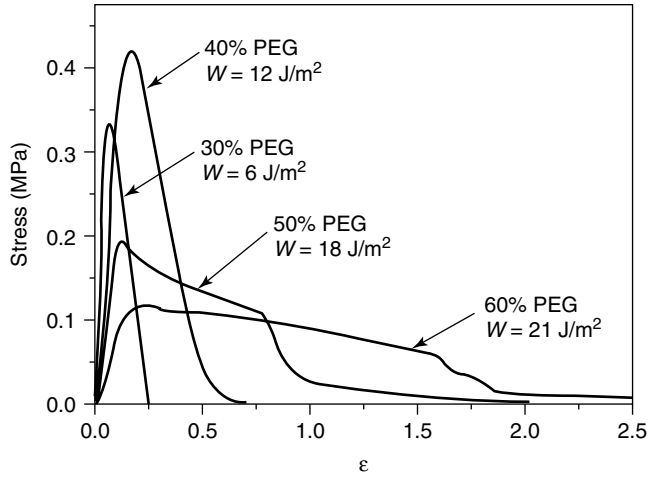


FIGURE 7.58 Effect of PEG-400 (wt %) on probe tack stress–strain curves of PVP–PEG–LLC system. The PEG concentrations in the blends are indicated; the contents of LLC (Eudragit L-100-55) and water are 8.33 and 12 wt %, respectively. The debonding rate is 0.1 mm/s. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol*., 21(7), 531, 2007. With permission.)

considered the tack.[3] Observed disagreement in the behaviors of the peak stress and the work of debonding indicates that the former value cannot always be accepted as an unequivocal characteristic of adhesion.

7.5.4.4 Effect of Absorbed Water on Adhesion

Another plasticizer that is compatible with the PVP–PEG–LLC system is water. Adhesion increases with blend hydration, going through a maximum at 17% for PVP–PEG–Eudragit L-100-55 blends (Figures 7.59 and 7.60). In contrast to the behavior of binary PVP–PEG blends (see Figures 7.40 and 7.41), the ternary PVP–PEG–LLC blends possess no initial tack. It is of great interest to compare the effects of water uptake on probe tack adhesion for PVP–PEG–Eudragit L-100-55 hydrogels (Figures 7.59 and 7.60) and Carbopol bioadhesives (Figures 7.4 and 7.5). The profiles in Figures 7.5 and 7.60 are remarkably similar, as are the positions of the adhesion maximum along the water sorption scale. The difference is quantitative: the work of debonding for Carbopol bioadhesives is 15–17 times lower than that for the PVP–PEG–Eudragit L-100-55 hydrogel.

Because the addition of LLC leads to a reduction in free volume and an increase in cohesion, it is not surprising that the carcass-like binary PVP–PEG complexes dissipate more detaching energy and demonstrate higher adhesion than the ternary PVP–PEG–Eudragit L-100-55 complexes combining the carcass-like and ladder-like types of noncovalent cross-linking (Figure 7.59). Note that the values of the practical work of adhesion, *W*, for ternary PVP–PEG–Eudragit L-100-55 blends are appreciably lower than those for binary PVP–PEG adhesives (compare Figures 7.60 and 7.41).

By comparing probe tack data in Figures 7.59 and 7.60, it is apparent that the effect of absorbed water on tack is similar to the effect of PEG-400. Whereas relatively dry

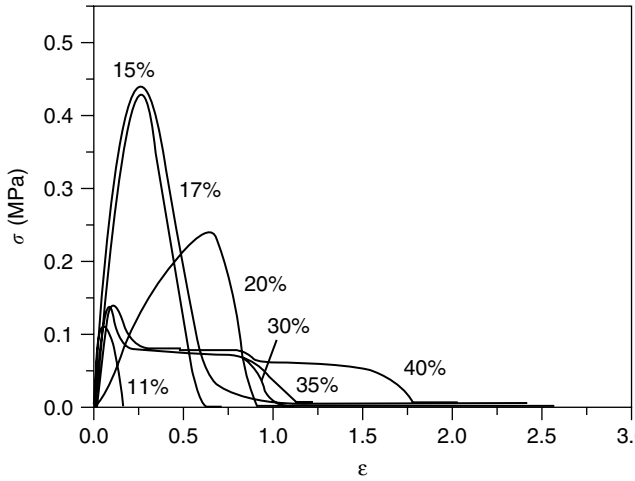


FIGURE 7.59 Effect of absorbed water (wt %) on probe tack stress–strain curves of PVP blend with 29 wt % PEG-400 and 12 wt % LLC (Eudragit L-100-55). The debonding rate is 0.1 mm/s. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

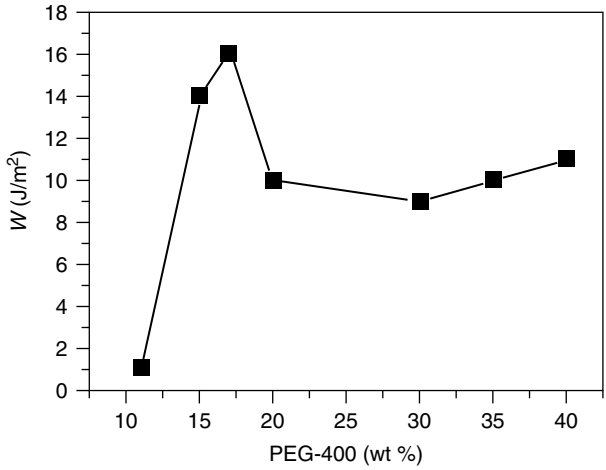


FIGURE 7.60 Effect of hydration on the debonding energy of the PVP–PEG–LLC complex. The debonding rate is 0.1 mm/s. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol*., 21(7), 531, 2007. With permission.)

PVP–PEG–Eudragit L-100-55 compositions (containing up to 11 wt % water) are initially nontacky and reveal a solid-like mechanism of debonding without fibrillation, adhesion increases with a rise in the content of absorbed water (Figure 7.60). With increasing hydration, tack passes through a maximum and stabilizes at a mild level as the swollen hydrogel blend becomes softer and more compliant. Such an adhesive profile is characteristic of bioadhesives that are designed to adhere to highly moistened biological tissues. A sharp transition to the deformation type demonstrates a pronounced plateau on the stress–strain curves and, in this manner, a well-expressed mechanism of fibrillation occurs between 7 and 11% absorbed water for binary PVP–PEG blends (Figure 7.40) and between 20 and 30% degrees of hydration for ternary PVP–PEG–Eudragit L-100-55 blends (Figure 7.59). In strong contrast to the behavior of conventional, hydrophobic PSAs, water behaves as an enhancer of adhesion both in binary PVP–PEG and in ternary PVP–PEG–LLC blends.

The ability of absorbed water to enhance significantly the adhesive properties of PVP–PEG–Eudragit L-100-55 blends, coupled with the lack of adhesion in comparatively dry blends and a high cohesive strength under extension, as well as the opportunity to manipulate adhesion and mechanical strength by simple varying of the blend composition, renders this composite especially suitable for many applications under aggressive action of surrounding moisture. The Corplex adhesive hydrogel films based on the PVP–PEG–Eudragit L-100-55 network complex retain their integrity, whereas most other bioadhesive materials fall apart upon hydration. Because of this difference, Corplex hydrogels do not leave a residue after being applied and removed from a substrate. Another advantage of the observed adhesive profile is the ease of handling of Corplex hydrogels over manufacturing, because in the dry state low tack prevents the hydrogels from sticking to machinery tools and packaging materials.

7.5.5 Solubility and Swelling of Adhesive Hydrogel Blends

7.5.5.1 Mechanism of Swelling

The mechanism of PVP–PEG–Eudragit L-100-55 blend swelling in water has been studied using the wedge microinterferometry (WMI) technique.[148] Principles underlying the WMI method have been described in detail elsewhere.[149,150] Briefly, this technique utilizes information provided by evolving interference fringe patterns of light transmitted through a sample, the thickness of which varies gently along one axis and whose composition varies perpendicular to that axis. Uniform samples exhibit equally spaced interference fringes perpendicular to the axis of increasing sample thickness, whereas composition gradients in the perpendicular direction cause sharp bending and crowding of the fringes. When all components of the polymer blend are soluble in the solvent, composition gradient and fringe density are high at early times following initial confrontation at the interface, but later relax to uniform composition, with an associated parallel fringe pattern. When some of the components are immiscible, however, a sharp phase boundary between the polymer and the solvent and dissolved components will appear. This phase boundary may block light transmission and will appear as a dark band in the interferogram. At equilibrium, parallel fringes are expected on both sides of the interface, but fringe spacings on the two sides will not be the same due to differences in the refractive index.

Typical WMI interferograms of the contact interface between PVP–PEG–Eudragit L-100-55 films and phosphate buffers at two pH values, 5.4 and 7.4, are illustrated in Figures 7.61 and 7.62. These pH values represent the nonionized and ionized states of the Eudragit L-100-55 component.

At pH 7.4 (Figure 7.61), the micrographs reveal interference patterns that are typical for systems with unlimited solubility. No phase discontinuity is seen, but a steep compositional gradient is inferred in the region where fringes are bent and crowded.

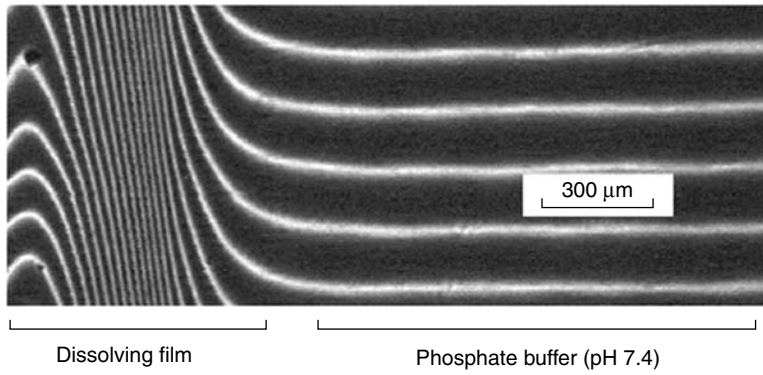


FIGURE 7.61 Microinterferogram of the contact interface between PVP (59%)–PEG (29%)–Eudragit L-100-55 (12%) film (left) and phosphate buffer (right); pH 7.4 (50 mM). Contact time is 2 min, $T = 36°C$. (From Bayramov, D.F., Singh, P., Cleary, G.W., Siegel, R.A., Chalykh, A.E., and Feldstein M.M., *Polym. Int.,* 59, 785, 2008. With permission.)

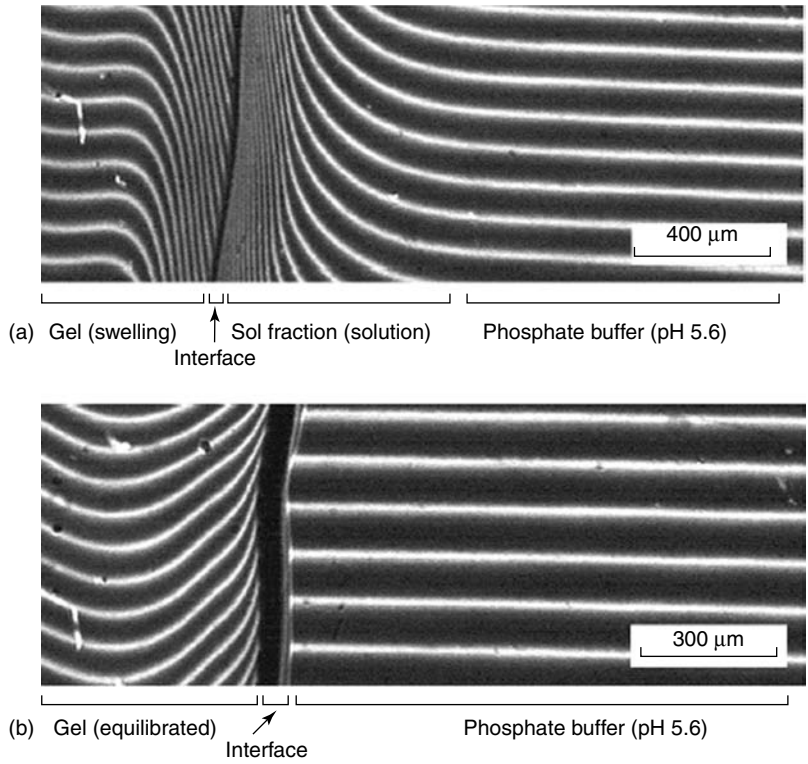


FIGURE 7.62 Microinterferogram of the contact interface between PVP (59%)–PEG (29%)–Eudragit L-100-55 (12%) film (left) and phosphate buffer (right), pH 5.6 (50 mM), at 36°C. (a) Contact time = 3 min. (b) Contact time = 20 h. (From Bayramov, D.F., Singh, P., Cleary, G.W., Siegel, R.A., Chalykh, A.E., and Feldstein M.M., *Polym. Int.,* 57, 785, 2008. With permission.)

This region, which corresponds to the dissolution zone, separates a region of nearly pure buffer (right) from the yet-undissolved hydrogel (left). Curvature in the fringes in the undissolved region is probably due to variations in composition resulting from the selection of components that dissolve at different rates. With time, the dissolution zone broadens as interdiffusion proceeds. At very long times, the sample composition will become uniform and display parallel fringes.

At pH 5.6 (Figure 7.62), the interference patterns display a sharp, persistent phase boundary indicative of immiscibility. At early stages (Figure 7.62a), there is rapid leaching of certain blend components, as evidenced by fringe bending/crowding near the phase boundary. At later stages (Figure 7.62b), the buffer appears to be of uniform composition, whereas a composition gradient remains in the hydrogel. In the latter case, slow leaching of soluble blend components from the gel is probably occurring, but these components equilibrate rapidly in the buffer. The nonmonotonic behavior of fringes on the hydrogel side is most likely due to the multiplicity of interdiffusing components.

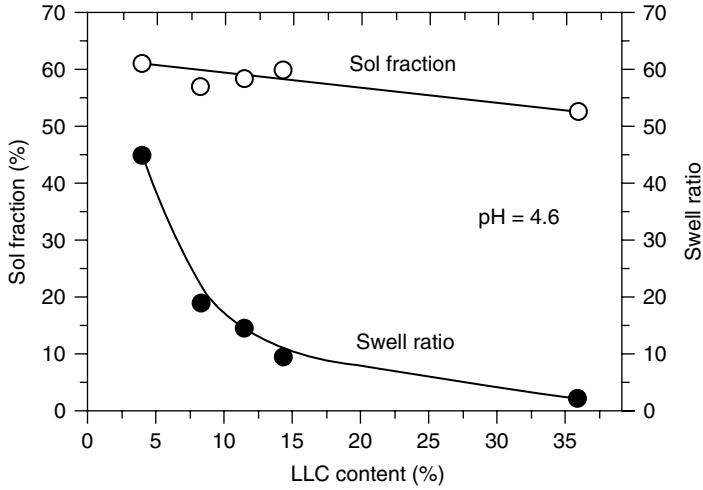


FIGURE 7.63 Effect of LLC concentration (Eudragit L-100-55) on swell ratio (SR) and sol fraction (SF) of a PVP blend with 50 wt % PEG-400. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

Thus, the microinterference patterns presented in Figures 7.61 and 7.62 illustrate clearly that the PVP–PEG–Eudragit L-100-55 blends behave like covalently cross-linked hydrogels over reasonably long time scales.

7.5.5.2 Effect of Ladder-Like Cross-Linker

The carcass-like PVP–PEG complex is easily soluble in water, whereas the ladder-like PVP complex with Eudragit L-100-55 is insoluble in aqueous media.[147] This behavior indicates clearly that junctions of the ladder-like network are much stronger and more stable under competitive action of water bonding than the junctions of the carcass-like network.

Besides the value of ultimate tensile stress, another measure of cross-linking density of the polymeric network is the swell ratio.[139] As illustrated by the data presented in Figures 7.63 and 7.64, both swell ratio and sol fraction decrease with increasing LLC concentration (Eudragit L-100-55 in Figure 7.63 or HPMCP in Figure 7.64).[147]

7.5.5.3 Impacts of pH and Poly(Ethylene Glycol) Concentration

Figure 7.65 illustrates the relationship between the fraction of PEG initially incorporated in the hydrogel and the fraction of polymer that is leached out as sol after 2 days. This sol fraction increases linearly with PEG content. From these graphs it can be concluded that the low-molecular-weight PEG is the primary component of the sol fraction. However, the sol fraction is always greater than the PEG fraction, indicating that other components such as low-molecular-weight PVP fractions are also leached, but to a lesser extent. Except for the lowest PEG fraction, the sol fraction is the same at pH 4.6 and 5.6. The sol behavior seen here differs from that seen when higher-molecular-weight PEGs are blended with PVP. It is evident that the stable three-dimensional hydrogen-bonded

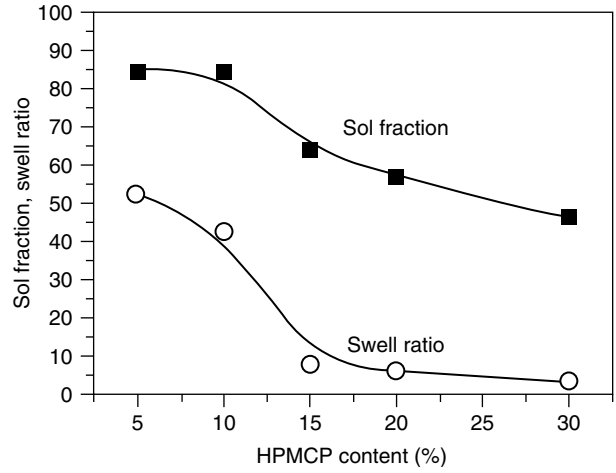


FIGURE 7.64 Swell ratio and sol fraction of PVP–PEG–HPMCP blends as a function of the content of LLC (HPMCP). (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

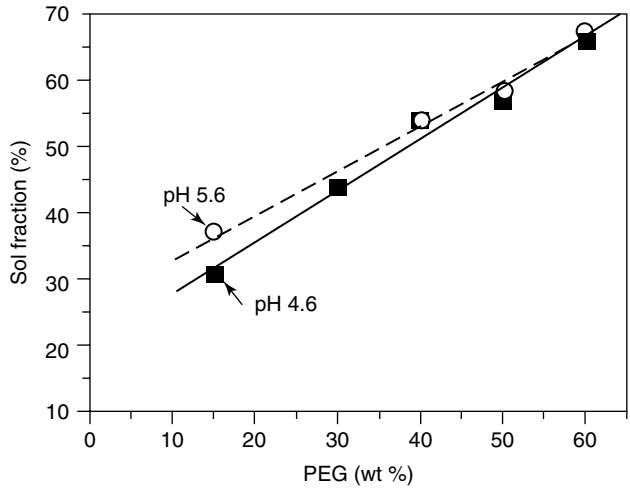


FIGURE 7.65 Relationship between the sol fraction of PVP–PEG–Eudragit L-100-55 blends and the content of PEG-400. [PVP]:[LLC] = 5:1. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol.*, 21(7), 531, 2007. With permission.)

network in the swollen state is formed predominantly between PVP and the Eudragit L-100-55 copolymer.

As illustrated in Figure 7.66, swelling of PVP–PEG–Eudragit L-100-55 blend after 2 days is pH dependent. The hydrogels swell 15- to 30-fold, with the PEG concentration only weakly affecting the swelling ratio. The swelling ratio increases appreciably

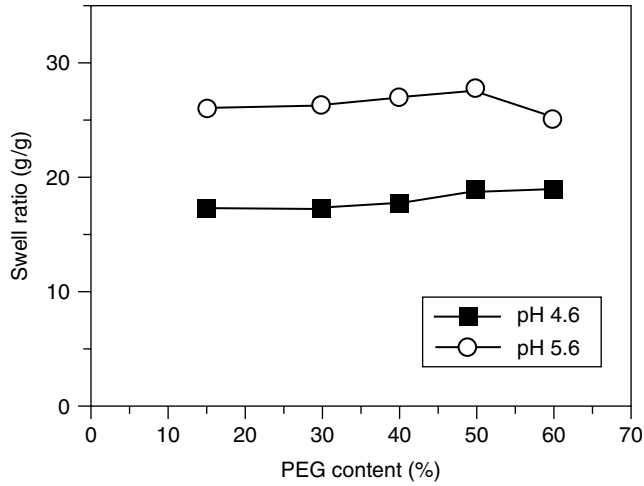


FIGURE 7.66 Effect of pH and PEG loading on PVP–PEG–Eudragit L-100-55 swelling. (From Bayramov, D.F., Singh, P., Cleary, G.W., Siegel, R.A., Chalykh, A.E., and Feldstein M.M., *Polym. Int.,* 57, 785, 2008. With permission.)

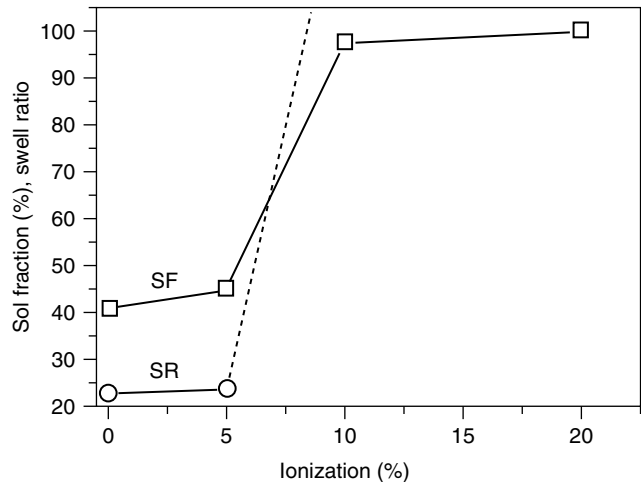


FIGURE 7.67 Effect of LLC (Eudragit L-100-55) ionization on swell ratio (SR) and sol fraction (SF) of PVP–PEG–LLC blends. (From Kireeva, P.E., Novikov, M.B., Singh, P., Cleary, G.W., and Feldstein, M.M., *J. Adhesion Sci. Technol*., 21(7), 531, 2007. With permission.)

at higher pH due to partial neutralization and ionization of Eudragit L-100-55 carboxylic groups present in the hydrogen-bonded hydrogel. Ionization of the carboxyl groups provokes swelling (Figure 7.67), in part due to the electrostatic/osmotic repulsion of polyelectrolyte chains and in part due to the loss of the carboxylic acid H-bond donor site. It is obvious that the same mechanism of Eudragit L-100-55 ionization governs the eventual dissolution of hydrogels at higher pH, as illustrated in Figure 7.61.

7.6 Corplex Adhesives of Controlled Hydrophilicity and Water-Absorbing Capacity

7.6.1 Noncovalently Cross-Linked versus Covalently Cross-Linked Hydrogels

Covalently cross-linked hydrogels have received much attention due to their permanence of shape, their elastic behavior under stress, and their ability to house, release, and serve as a medium for controlled permeation of active substances. Unfortunately, covalently cross-linked hydrogels have not been applied as broadly as was hoped in the biomedical arena. One limiting factor has been the difficulty in guaranteeing removal of impurities such as unreacted monomers, sol fractions, nonaqueous solvents, and initiators. A second limitation is that once the three-dimensional covalent network is formed, it cannot be readily processed.

The PVP–PEG–LLC hydrogen bonded networks described in this section behave like covalently cross-linked hydrogels. In terms of their adhesive properties, they bridge the gap between PSAs and bioadhesives, combining the strength of adhesive joints featured for PSAs with the ability to adhere to wet substrates typical of bioadhesives, based on covalently cross-linked hydrogels. The components are all of pharmaceutical grade, and the blends can be formed without introduction or formation of toxic by-products. Moreover, because the hydrogen-bonding interactions that form the network are reversible, the blends are much more readily processed by controlling temperature, solvent choice, etc. The materials are malleable under various processing conditions such as drawing, molding, and extrusion. Therefore, the blends appear to present several advantages from the manufacturing and regulatory points of view. The Corplex adhesive hydrogels based on the FFP–CLC–LLC complexes are currently available from Corium International.[151,152]

7.6.2 Hydrophilicity of Corplex Adhesives

As evident from the results presented in Section 7.6.1, Corplex technology based on the molecular design of PSA materials offers products with varying adhesion, mechanical, and water-absorbing capabilities. The technology provides a convenient tool for obtaining the desired material performance by simply varying the composition of polymer blends. The values of swell ratio, SR, and sol fraction, SF, can be used as a basis for the classification of Corplex adhesives in terms of their hydrophilicity. The higher the SR and SF values, the higher the hydrophilicity of the adhesive and the lower the density of noncovalent cross-linking. The binary blends of PVP–PEG demonstrate SF = 100% and the value of SR tends to be infinitesimally high. Conventional hydrophobic PSAs such as acrylic Duro-Tak 87-900A and SIS-based Duro-Tak 387 2287 adhesives fall on the other side of the scale of hydrophilicity (SF $\approx$ 0% and SR $\approx$ 0.1). This means that the percentage of their water absorbency (defined in grams of water absorbed per 1 g of dry material at 25°C and 100% relative humidity) does not exceed 10%.

The Corplex adhesives fill the range between these two extremes of the scale of hydrophilicity (Figure 7.68). The SR scale is used in Figure 7.68 to classify the Corplex adhesive absorbents in four broad categories.[109]

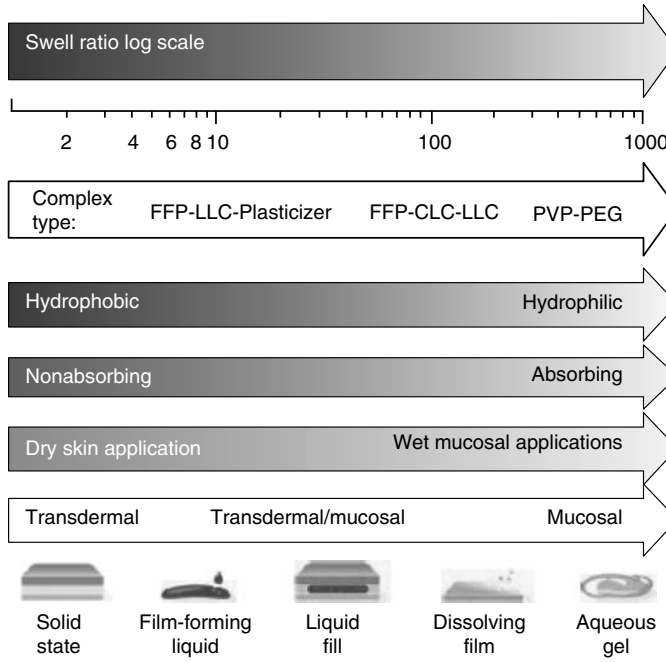


FIGURE 7.68 Classification guide of Corplex® adhesives outlining basic polymer complex structure and corresponding adhesive properties and potential applications.

Water soluble adhesives comprise the Corplex-100 series. The PVP–PEG blends are included in this series of adhesive composites, along with plasticized FFP–LLC polyelectrolyte complexes and FFP–CLC–LLC blends involving ionized macromolecules of FFP and LLC.

Superabsorbent (SA) adhesives have values of water absorbency from 1,000 to 10,000% (SR $\approx$ 10–100). Typical representatives of this category are the FFP–CLC–LLC complexes exemplified by PVP–PEG–Eudragit L-100-55 and PVP–PEG–HPMCP blends, which contain comparatively small amounts of LLC. These adhesive absorbents are called the Corplex-200 series. As follows from the data illustrated in Figures 7.63 and 7.64, depending on the blend composition, this type of adhesive absorbent has SR values in the range from 53 to 2.3, whereas SF varies between 85 and 46%. The interpolymer complexes of the FFP–LLC–plasticizer type, known as adhesive absorbents of the Corplex-700 series (see below), which include as LLC a highly hydrophilic copolymer of maleic acid with methylvinyl ether, PMA-co-MVE, demonstrate SR and SF values between SR = 89–16 and SF = 76–44%, respectively (Figure 7.34).

Medium absorbent (MA) adhesives have values of water absorbency from 200 to 1,000% (SR ranges from 2 to 10). Along with densely cross-linked Corplex-200 adhesives based on the FFP–CLC–LLC interpolymer complex, this class of adhesive absorbents also includes the plasticized FFP–LLC complex described

in Section 7.3. The FFP–LLC–plasticizer complex constitutes mainly the Corplex-700 series of adhesive absorbents. As follows from the data illustrated in Figures 7.28 and 7.30, the plasticized Eudragit E-100 complexes with Eudragit L-100-55 demonstrate SR and SF values varying within the ranges of SR = 6.3–2.3 and SF = 76–44%. Adhesive absorbents in the MA category may also be prepared by mixing conventional hydrophobic PSAs with hygroscopic polymer absorbents, such as covalently cross-linked PVP, PAA, agar, etc. The polymer composites of this type are known as hydrocolloids and fall into the Corplex-500 series of adhesive absorbents, the description of which is beyond the framework of present review.

Weak absorbents demonstrate water absorbency ranging from 100 to 200% (SR ≈ 1–2). In addition to conventional hydrophobic PSAs, which are not described in this review, typical representatives of this category of adhesive absorbents are mixtures of plasticized FFP–LLC complexes with acrylic PSAs.[109]

7.6.3 Corplex Adhesive Absorbents Compared with Conventional Pressure-Sensitive Adhesives and Bioadhesives

This chapter introduces a new hydrophilic PSA technology developed by Corium International, Inc., termed Corplex. Corplex adhesives provide the high water absorbing capacity associated with bioadhesives and the adhesive properties of traditional hydrophobic PSAs. This class of adhesives has high adhesive strength to both dry and moist substrates and the ability to absorb water while still maintaining PSA properties.

As follows from the data listed in Table 7.5[110], the properties of Corplex adhesives bridge the gap between conventional PSAs and typical bioadhesives. Figure 7.69 compares the peel adhesion toward dry and moistened human forearm skin *in vivo* of conventional acrylic PSA with three grades of Corplex adhesives: (1) a plasticized ladder-like complex exemplified by Eudragit E-100–Eudragit L-100-55–TEC blends (Section 7.3), (2) the carcass-like PVP–PEG complex (Section 7.4), and (3) the FFP–CLC–LLC complex (e.g., PVP–PEG–Eudragit L-100-55–TEC, Section 7.5). According to these data, the adhesive properties of Corplex polymer composites share the properties of PSAs and bioadhesives by combining the high adhesion characteristic of conventional PSAs with the ability to adhere to moistened skin and biological tissues typical of bioadhesives.

In Figure 7.70, the probe tack behaviors of the water-soluble PVP–PEG adhesive, the PVP–PEG-LLC adhesive, and the amphiphilic FFP-LLC adhesive plasticized by TEC and containing tackifier (T) rosin are compared with the properties of two different grades of conventional PSAs. Expressed in terms of maximum stress under debonding, the tack of Corplex adhesives is comparable to that of typical PSAs. However, the distinctive feature of the adhesive blends, as illustrated in Figure 7.70, is the lower value of maximum elongation due to noncovalent cross-linking of the chains of FFPs. Because the CLC is significantly looser than the LLC, it is no wonder that the water-soluble PVP–PEG adhesive demonstrates higher elongation at probe detachment than the adhesives involving ladder-like cross-linking.

TABLE 7.5 Comparison of CORPLEX-100™ and -200™ Series Adhesives with Conventional PSAs (e.g., Duro-Tak®, 34-4230 based on styrene–isoprene–styrene (SIS) triblock copolymer) and Typical Bioadhesives (acrylic acid polymers Carbopol® and Noveon®)

Attribute	PSA	Bioadhesives	PVP–PEG	PVP–PEG–LLC	FFP–LLC + Plasticizer
Peel adhesion (N/m)					
In dry state	300–600	None	50–70	10–30	200–610
In hydrated state	None	10–60	300–550	100–300	140–570
Debonding work (J/m^2)	30–300	0.1–1.1	29–140	12–48	29–45
Sol fraction (%)	0–10	60–95	100	40–85	3–76
Swell ratio	1.0–1.5	10–95	None	2.3–89	2–10
Film-forming capacity	Yes	No	Yes	Yes	Yes
Elastic modulus (MPa)	0.1–0.5	0.01–0.07	0.13–1.2	0.04–4	0.1–0.7
Maximum elongation	22	>30	22	2.7	1.7
Ultimate tensile strength (MPa)	16	0.01	12	30.4	5

Source: From Cleary, G.W., Feldstein, M.M., and Beskar, E., *Bus. Briefing*, *Pharmatech*, 1, 2003. With permission.

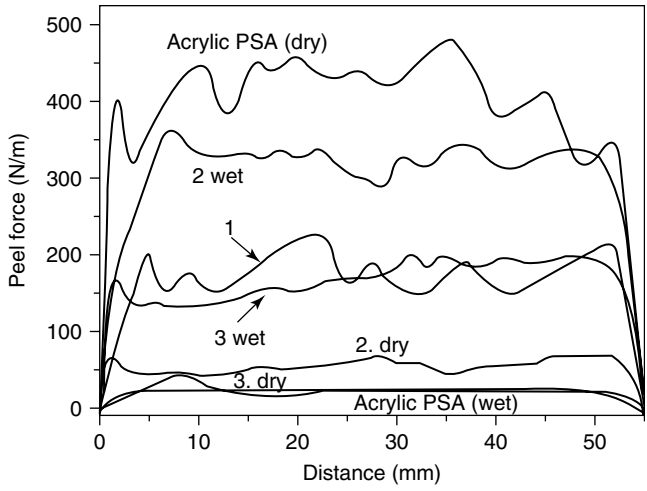


FIGURE 7.69 Peel force traces toward dry and wet human skin for Gelva acrylic PSA, amphiphilic adhesive based on plasticized ladder-like FFP-LLC complex (1), water-soluble adhesive based on carcass-like PVP–PEG complex (2), and hydrophilic PVP–PEG–LLC adhesive (3). (From Feldstein, M.M., Cleary, G.W., and Platé, N.A., In: *Developments in Pressure-Sensitive Products*, 2nd ed., Taylor & Francis, New York, 2005, ch. 9. With permission.)

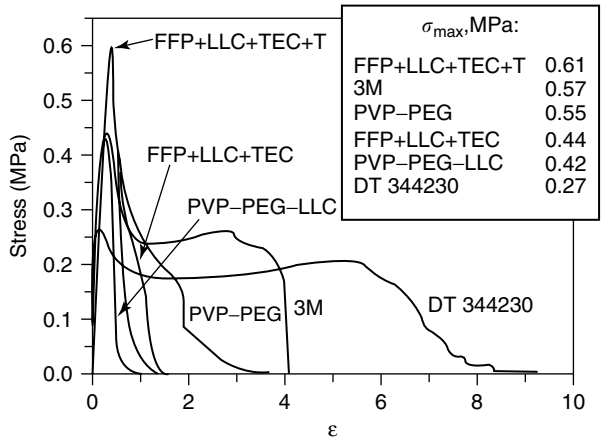


FIGURE 7.70 Probe tack stress–strain curves for water-soluble PVP–PEG (36%) adhesive, amphiphilic adhesives FFP–LLC–TEC (35%) and FFP–LLC–TEC (30%) + 7% tackifier (T), and hydrophilic PVP–PEG–LLC adhesive at 17% absorbed water in comparison with two grades of conventional PSAs: SIS-based Duro-Tak® 34-4230 and acrylic PSA manufactured by 3M. (From Feldstein, M.M., Cleary, G.W., and Platé, N.A., In: *Developments in Pressure-Sensitive Products*, 2nd ed., Taylor & Francis, New York, 2005, ch. 9. With permission.)

7.7 Outlook and Conclusions

For a number of practical purposes, it would be useful to have a range of pressure-sensitive and bioadhesive polymeric materials with different hydrophilicity. For some time, attempts have been made to combine the properties of hydrophobic PSAs and hydrophilic bioadhesives. The traditional line of attack has been through hydrophilization of hydrophobic adhesives by their physical or chemical modification. Although some published examples of hydrophilic PSAs obtained by either blending of hydrophobic PSAs with hydrophilic polymers or grafting/copolymerization techniques exist, reviewed in Sections 7.1.2, 7.1.3, and 7.1.4.3, no published data demonstrate adhesives that possess both the properties of a traditional PSA and the characteristics of a traditional bioadhesive.

The ideal situation would therefore be to develop a wide range of hydrophilic PSAs that combine the properties of conventional PSAs and bioadhesives and that can be used in a number of applications including, but not limited to, transdermal, transmucosal, and topical drug delivery systems. In addition, the adhesive compositions should also be compatible with active agents of varying hydrophilicity, hydrophobicity, and molecular structure.

Nature has created no such hydrophilic adhesives, but fortunately, recently developed molecular insight into the origins of pressure-sensitive adhesion (see *Fundamentals of Pressure Sensitivity*, Chapter 10)[27] instructs us regarding how hydrophilic adhesives may be made by blending nonadhesive hydrophilic polymers. In particular, this can be achieved by the formation of interpolymer complexes provided by ionic, electrostatic, or hydrogen bonding between electron-donating and electron-accepting polar functional

groups in the macromolecules of hydrophilic polymers. Polymer components of the blends become reversibly cross-linked into a network of supramolecular structures, which results in coupling of high cohesion with large free volume, a necessary condition for pressure-sensitive adhesion to occur.

Based on such a pioneering advanced molecular design method, hydrophilic PSAs have now been obtained for the first time that encompass the entire range of hydrophilicity and water-absorbing capacity from water-soluble to water-insoluble and amphiphilic PSAs. Among these adhesives, there are materials that share the high tack typical of hydrophobic PSAs with the ability to enhance adhesion in the course of moistening, a property of classical bioadhesives. The complex of water-absorbing, elastic, and adhesive performance properties of hydrophilic polymeric blends may be easily controlled by varying their composition, in which every component of the blend has its own clearly defined function. Thus, the concentration of noncovalent cross-linker is an effective tool to control the cross-linking density and provide the necessary cohesive strength of the material, whereas the concentration of plasticizer mainly governs ductility and tack. The chemical nature of the FFP that is present in the composition in the highest concentration affects the dissolution, swelling, and water-absorbing capacity of adhesive polymer blends.

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8

Role and Methods of Formulation

8.1 Adhesion-, End-Use-, and Technology-Related Formulation **8**-3
Adhesion-Related Formulation • End-Use-Related Formulation • Product Construction-Related Formulation • Raw Material-Related Formulation • Technology-Related Formulation

8.2 Formulation Methods **8**-39
Tackification • Cross-Linking • Filling • Formulation with Additives • Formulation of Other Coating Components

8.3 Progress in the Formulation of Pressure-Sensitive Adhesives **8**-67
Plastics-Based Pressure-Sensitive Adhesives • Advances in Elastomers • Advances in Cross-Linking

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As discussed in Chapter 1 for pressure-sensitive adhesive (PSA) converters, the manufacturing method of the adhesive is generally based on its formulation. PSAs are based on macromolecular compounds and the main part of these compounds is synthesized by the chemical industry (see also Chapter 1). Some are elastomers (see also Chapters 2 through 4 and 7), whereas others are viscoelastomers (see also Chapters 4 through 7) or have viscous components (see also Chapter 4). Elastomers must be transformed into viscoelastomers; raw viscoelastomers must be tailored according to their end use. Their processing depends on the coating technology, equipment, carrier material, end use, and economic considerations. This processing step, as well as their storage, application/deapplication, and recycling (see Chapter 10 and *Applications of Pressure-Sensitive Products*, Chapter 4) require modification of the properties of the raw materials employed. This is the role of formulation [1]. Formulation is more than a blending of adhesive components. It begins with the design of the pressure-sensitive raw material (polymer) and continues as a range of chemical and physical processes determined by chemical technology. This technology is also based on mixing. Some compounds used for in-line

adhesive synthesis (see Chapter 1) require multiple formulations to achieve a coatable intermediate, which is designed for postcoating reactions. Therefore, the manufacture of the adhesive and adhesive components includes their synthesis and formulation.

For most PSAs, formulation is the final manufacturing step, yielding a product with the required processing and end-use properties. However, the end-use properties may differ according to product class (see *Applications of Pressure-Sensitive Products*, Chapter 1). For different pressure-sensitive products (PSPs), various raw materials, formulating components, and formulating technology have been suggested. The formulation of PSAs for PSPs consists of numerous special features.

The aim of formulation and its modalities varies widely depending on the raw materials used. PSAs based on natural rubber (NR) and synthetic elastomers must be formulated with viscous components to achieve viscoelastic behavior and adequate pressure-sensitive properties. The formulation of viscoelastic pressure-sensitive raw materials is only tailoring of the PSA (i.e., modifying a given "finished" adhesive to achieve other adhesive, conversion, or end-use properties). Formulation is the manufacture of the adhesive by mixing various components. A variety of PSPs are manufactured using various coating techniques, carrier materials, and construction (see Chapter 10 and *Applications of Pressure-Sensitive Products*, Chapters 1 and 4). Economic considerations also limit the use of certain raw materials. The build-up of a PSP from a PSA and its solid-state components (carrier and release liner) requires the PSA to have certain coating and converting (lamination, confectioning, etc.) properties (see also Chapter 10 and *Applications of Pressure-Sensitive Products*, Chapters 4 and 8). Thus, formulation depends on the adhesion, end-use, and technological characteristics of the adhesive. The design and formulation of PSAs were described in detail in our previous works [1–3], and the formulation of the solid-state components of PSPs was discussed in detail by Benedek in Refs [4,5]. The fundamentals of pressure sensitivity as the relate to pressure-sensitive design were discussed by Benedek in Ref. [3] and by Feldstein in Refs [6,7]. In *Fundamentals of Pressure Sensitivity*, interfacial and rheologic processes are considered the main features of pressure sensitivity (*Fundamentals of Pressure Sensitivity*, Chapter 1), and the role of diffusion in adhesion (*Fundamentals of Pressure Sensitivity*, Chapter 2) and of transition zones is investigated (*Fundamentals of Pressure Sensitivity*, Chapter 3). The rheology of PSAs and PSPs was discussed in our previous works [8,9], where the rheology of the carrier material, adhesive PSA solutions and dispersions, and abhesive and PSPs (labels, tapes, and protection film, i.e., pressure-sensitive laminates) were investigated from the practical point of view in correlation with the mechanical properties. The rheology of the coated adhesive and its parameters, the rheology of reinforced systems, the interdependence of rheology–adhesive characteristics, rheology during processing, and the energetic aspects of rheology were also discussed by Benedek [9]. The influence of viscoelastic properties on the adhesive properties of PSAs and the converting properties of PSAs and PSPs, as well as the factors influencing the viscoelastic properties, were examined. Advances in the study of the viscoelastic properties of PSAs and their viscoelastic behavior during bonding and debonding are examined by Derail and Marin in *Fundamentals of Pressure Sensitivity*, Chapter 4, and the role of viscoelastic windows is discussed by Chang in *Fundamentals of Pressure Sensitivity*, Chapter 5. Advances in contact physics and the mechanics of viscoelastic materials allowed the correlation of

macromolecular characteristics to the mechanical properties of the polymers and the bonding/debonding mechanism. The basis for viscoelastic adhesion on solid surfaces was laid by Creton and Leibler [10]. In the past decade appreciable progress has been achieved in the quantitative description of the micromechanics of PSA debonding [11,12]. These works consider nucleation of cavities within the pressure-sensitive polymer and extension of fibrils the major factors leading to the dissipation of applied energy. For a material that obeys the simple kinetic theory of rubber elasticity, the critical pressure at which the cavity will grow without limit is proportional to the initial elastic modulus of the material. Dahlquist's criterion correlates pressure sensitivity to the modulus values. Thus, taking into account the correlation of macromolecular characteristics (e.g., free volume and cohesion) to pressure sensitivity by Feldstein and colleagues [6,7,13], a theoretical basis was given for Dahlquist's empiric criterion of a critical modulus value and to the industrial practice of pressure-sensitive bonding/debonding (measured by tack and peel resistance). Advances in contact mechanics and bonding/debonding theory, which take into account diffusion and relaxation phenomena, are presented in *Fundamentals of Pressure Sensitivity*, Chapters 2, 3, 6, 9, 10, and 11.

This chapter serves as a guide to understand the use of the PSA raw materials described in Chapters 1 through 9 and their formulation. In practice, formulation is a processing step included in the manufacture of PSAs and PSPs. Formulation technology is summarized in Chapter 10 as it regards the manufacture of PSAs and PSPs. Formulation plays a decisive role in the choice of manufacture and converting technology of PSPs (see Chapter 10) and in the end-use properties and application technology of PSPs (see *Applications of Pressure-Sensitive Products*, Chapter 4).

8.1 Adhesion-, End-Use-, and Technology-Related Formulation

In principle, the scope of formulation is to develop a recipe with properties tailored to the product's end-use. One of the most important end-use criteria is adhesive quality, evaluated as the sum of the adhesive performance characteristics. As mentioned previously, formulation must allow the use of the adhesive to manufacture of PSPs (ensuring adequate coating and converting properties) and to enhance the application of the final product (converting and other end-use properties). Ideally, the scope of the formulation is to fulfill the requirements of the entire spectrum of performance properties. Formulation gives priority to well-defined requirements. The adhesion of a PSA, characterized by its special adhesive properties, is the most important requirement.

The role and principles of formulation were discussed in detail by Benedek in previous books [13,14] and its material basis was described by Benedek in Ref. [15]; the industrial aspects of formulation were discussed by Benedek in Ref. [16]. As noted, formulation influences the global manufacture technology of PSPs, as well as the global product technology (i.e., the product-application technology). As discussed in Chapter 1, synthesis of the pressure-sensitive raw material requires a monomer-based design and formulation (except in-line synthesis, in part). Tailoring of the synthesized (or natural) pressure-sensitive raw materials is based on polymers. The main role of formulation is to ensure the

TABLE 8.1 Scope of Formulation

General Scope of Formulation	Special Segments	Parameters
Formulation for manufacture of PSPs	Formulation for PSA coating technology	Coating equipment Productivity Environmental considerations
	Formulation for PSA manufacture and processing technology Choice of PSA processing technology	Choice of PSA manufacturing technology Coatability Drying Running speed
	Formulation for PSA and PSP converting	Converting properties Confectioning properties
Formulation for application and end-use of PSPs	Formulation for adhesive properties Formulation for specific properties	Product class and grade Economic considerations Application domain

pressure-sensitive character of a recipe related to its end use and to allow the manufacture of PSPs based on this recipe. The scope of formulation is summarized in Table 8.1.

8.1.1 Adhesion-Related Formulation

The main purpose of formulation is to regulate the adhesion–cohesion balance. Practically, it is an attempt to achieve the required tack, peel resistance, and bond-break characteristics, assuming that the formulated adhesive preserves the internal cohesion required for its conversion and end use. Therefore, in principle, the formulation for adhesive properties of a common (label grade) PSA consists of its tackification or detackification. Although the raw adhesive possesses sufficient cohesion before tackification, improvement of its tack and peel by compounding with a tackifier resin or a plasticizer may cause a pronounced decrease in shear resistance (see Section 8.2). The level of shear resistance required for balanced adhesion can be restored through the addition of other formulation components to the recipe (e.g., high-melting-point resins, hard PSAs, or cross-linkable components). Formulation for adhesion supposes know-how about adhesive properties and their characterization and about the influence of various raw-material-related, manufacture-technology-related, and product build-up-related parameters. The adhesive properties of PSAs were described in detail in our previous works [17–19]. The main parameters of pressure-sensitive adhesion and their balance for various PSPs were discussed by Benedek in Ref. [18], where the definition and characterization of adhesive properties (common and special adhesive performance) and their regulation by means of the adhesive, carrier, manufacture technology, and product application technology are described. In this book the special adhesive performance- (e.g., application tack, removability) and product class- (e.g., label, tape, protection film) dependent properties are discussed in a detailed manner. The role of the adhesion–cohesion balance is described by Benedek in Ref. [17]. The control parameters of the adhesive properties are listed in Table 8.2. The parameters are synthesis or formulation related.

TABLE 8.2 Control Parameters of the Adhesive Properties

PSA Raw Material	Adhesive Properties (Positive Changes)		
	Tack	Peel Resistance	Shear Resistance
NR	Mastication Tackification	Mastication Cross-linking Tackification	Cross-linking
CSBR	Butadiene level (50–70%) Tackification	Styrene/butadiene ratio (Adhesive failure at low butadiene level) Molecular weight, MWD Cross-linking	Styrene level Molecular weight Cross-linking
SBC	Diene/styrene ratio Tackification Di-block/triblock ratio	Styrene/diene ratio Tackification	Tackification
AC	Molecular weight Tackification	Acrylic acid content Adhesive failure at critical fraction of EHA Cross-linking Tackification	Acrylic acid content Cross-linking Filling

The scope of formulation differs according to product class. With the exception of special requirements and products, PSAs for labels are formulated to achieve better peel resistance and tack. PSAs for tapes are formulated to obtain better shear resistance and PSAs for protective films to realize better removability. Thus, the ideal adhesion–cohesion balance is different for labels, tapes, and protective films; therefore, the scope of formulation for adhesive properties and the formulation possibilities for such products also differ. In Ref. [16] the design and formulation for adhesive properties is described by Benedek according to product classes (labels, tapes, and protection films).

8.1.1.1 Balanced Formulation

PSAs possess adhesion for bonding and debonding and the cohesion necessary against debonding. The special balance of these properties, the adhesion–cohesion balance, embodies the pressure-sensitive character of the adhesive. In relation to their application technology (labeling) and end use, permanent labels need a balanced formulation [i.e., high instantaneous adhesion (tack), high delamination resistance (peel resistance), and (as related to their converting technology) acceptable cohesion (shear resistance)]. The fundamentals of such adhesive characteristics are described in detail in *Fundamentals of Pressure Sensitivity*, Chapters 6 through 8. The practice of characterization of adhesive properties is discussed in *Applications of Pressure-Sensitive Products*, Chapter 8. The notion of balanced formulation refers to a formulation yielding "usable" adhesive properties with a common coating weight of ca. 20 g/m^2. In this case, "usable" means an adhesive-coated product with a permanent bond caused by low pressure, instantaneous application after a standard dwell time, and common processibility (convertability) of the PSP.

As noted in Ref. [14], formulation for mixing includes tackification/detackification and cohesion regulation. Formulation methods include tackification, plasticization, cross-linking, filling, depolymerization, etc. (see Section 8.2.1). Tack and peel resistance are regulated by tackification (see Section 8.2.1.1). It should be taken into account that tack and peel resistance do not improve (always) in parallel. The required tackifier level depends on the base elastomer, the nature (chemical and physical status) of the tackifier, and the tackifying technology, and the interdependence of peel resistance–shear resistance influences the level of the debonding force and the type of failure. For common labels, the formulation criteria imposed by their end use depend on whether the labels will be produced on reels or sheets (see Chapter 10 and *Applications of Pressure-Sensitive Products*, Chapter 1) and on whether the product is to be permanent or removable (see *Applications of Pressure-Sensitive Products*, Chapter 1).

It should be noted that adhesive formulation, together with coating weight and coating technology, determine the balance of adhesive performance characteristics. As discussed in Ref. [18], regulation of the adhesive properties with the adhesive includes changes in the composition of the PSA or in the structure and geometry of the PSA. The adhesive properties depend on the area of contact between the adhesive and substrate, which is also a function of adhesive geometry. Adhesive geometry is characterized by the continuous or discontinuous character of the coated layer (see Chapter 10) and the coating weight. An increase in coating weight improves tack and peel and decreases removability. For instance, mounting, insulating, and splicing tapes possess coating weight values higher than 30 g/m^2; removable tapes, like protective films, are coated with less than 10 g/m^2 adhesive (see *Applications of Pressure-Sensitive Products*, Chapter 4). The role of coating weight and the parameters influencing it were examined by Benedek in Ref. [17]. Coating weight affects the geometry and quality of the coated adhesive layer. Its influence on the quality of the PSA layer is indirect through drying. The coating weight influences the drying of the adhesive layer. Generally, the drying rate is inversely proportional to layer thickness. The influence of coating weight on drying has an indirect effect on adhesive characteristics. The equilibrum–water content of the paper carrier and water-based PSA layer depends on the drying degree (i.e., the coating weight). Residual humidity affects tack, peel resistance, and shear resistance.

The most important factors influencing coating weight are the carrier material, the adherent, the permanent/removable character of the adhesive, PSP build-up, and the coating conditions. Figure 8.1 illustrates the influence of the carrier material (its bulk and surface properties) on the adhesive and converting properties of PSP directly and via coating weight.

The optimum coating weight value depends on the chemical composition and the end use of the PSA. The coating weight must be correlated to the uniformity of the coated layer and to the coating (film-forming) quality, depending on the machine characteristics and adhesive characteristics (for more information on the influence of coating weight on the adhesive and conversion properties and its dependence on PSP construction, see *Applications of Pressure-Sensitive Products*, Chapter 8). Machine characteristics include the speed and sense of rotation of the metering cylinders, concentricity of the rolls, gap width, properties of the rolls (e.g., surface finish, deflection), configuration, number and combination of rolls, hydraulic pressure, and temperature control (see also Chapter 10).

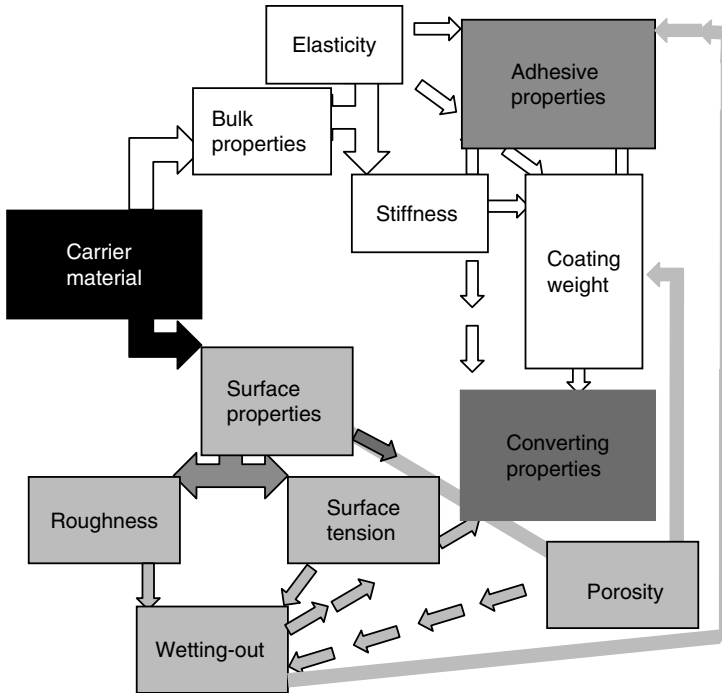


FIGURE 8.1 The influence of the carrier material on the adhesive and conversion properties of PSPs.

Adhesive characteristics include cohesive strength, flow, and rheologic properties. According to their chemical nature, synthesis, or formulation, various adhesives possess a different adhesion–cohesion balance, which can be shifted by increasing the coating weight. The most important parameter in coating technology that influences the coating weight is the direct/indirect nature of coating (see also Chapter 10). A detailed analysis of the influence of coating conditions (coating technology) on coating weight was presented by Benedek in Ref. [20]. Generally, the choice of a coating device depends on the desired coating weight range, changes in coating weight, and uniformity of the coating weight. The dry coating weight (i.e., the weight of the dry adhesive applied per unit surface area) can vary substantially, depending upon the porosity and irregularity of the carrier material and the adherent. For instance, a good adhesion for tapes manufactured from continuous polymeric materials can usually be achieved with dry adhesive coating weights of about 15–30 g adhesive/m^2, whereas paper-backed tapes use 16–30 g/m^2 PSA and tapes with textile carrier material have a coating weight of about 40 g/m^2. The anchorage of the adhesive on the carrier influences the coating weight as well. For instance, primed, removable products work with less coating weight [18]. The conformability and deformability of the face stock material also affects the coating weight (see also Chapter 1 and *Applications of Pressure-Sensitive Products*, Chapter 4). For instance, a soft and thin low-density polyethylene carrier for protection films requires lower coating weight values than high-density polyethylene (HDPE) or

polyethylene terephthalate (PET). As mentioned previously, the adherent (substrate) influences the coating weight as well. Its chemical nature (e.g., affinity and polarity) and physical nature (e.g., porosity and roughness) affect the adhesive–substrate interaction. As an example, in the correlation given by Tordjeman et al. [21] for the contact area (A_c) as a function of the contact force, F_c, in probe tests (see *Fundamentals of Pressure Sensitivity*, Chapter 6, and *Applications of Pressure-Sensitive Products,* Chapter 8), the apparent modulus, E_a, takes into account the competition between the thickness effects and roughness (a).

$$A_c \approx N\pi(a)^2 + \beta F_c/E_a \tag{8.1}$$

Hui et al. [22] mathematized the influence of the asperities (aspect ratio and number of asperities) on self-adhesion.

The influence of adhesive geometry on peel resistance was examined in detail by Benedek in Ref. [17] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). As noted, a reduction in coating weight to values under the critical coating weight causes joint failure. In principle, such a reduction may be the result of carrier (and adhesive) deformation [23] (see also Chapter 1). According to Williams and coworkers [24], the current challenge is to model accurately any extensive plastic deformation that may occur in the flexible peeling arm, because if this is not accurately modeled, then the value of G_c (fracture energy) may suffer a high degree of error.

As discussed in Chapter 1, due to the composite (laminate) construction of PSPs, their behavior must be examined as a whole, because debonding may arise as the sum of plastic deformations (flow) of the adhesive as well as of the carrier material.

8.1.1.2 Unbalanced Formulation

Unbalanced formulations ensure higher adhesion-related or cohesion-related performance characteristics. For unbalanced formulations required for special labels and tapes, tack and peel resistance (e.g., special labels) or peel resistance and shear resistance (e.g., tapes) are increased in comparison with other adhesive characteristics. For such products tack can be improved by using a higher coating weight; tack can be decreased by cross-linking or detackification (see also Sections 8.2.1 and 8.2.2); peel resistance and shear resistance can be augmented by cross-linking. Although labels can have an unbalanced formulation as well (e.g., removable labels), it is more typical for tapes and protective webs. For tapes the adhesive must resist dynamic loads (e.g., packaging, closure, mounting and splicing tapes; see *Applications of Pressure-Sensitive Products*, Chapter 4); thus, a high-cohesion formulation is required. Adhesive for protection films requires a composition without tack (the product is laminated under pressure; see *Applications of Pressure-Sensitive Products*, Chapters 4 and 7); therefore, there is no need to achieve an adhesion–cohesion balance. More important is the low peel resistance ensured by cross-linking and a low coating weight. For instance, for removable protection films, peel values of 0.3–1.3 N/25 mm are recommended (see also *Applications of Pressure-Sensitive Products*, Chapter 4). For such products the coating weight is situated between 0.5 and 1.5 g/m^2 (with a coating tolerance of $\pm$0.5 g/m^2). Removable formulations as a special case of unbalanced formulation will be discussed in Section 8.2.3.

8.1.1.2.1 Formulation for Tack and Peel Resistance

As discussed in detail by Benedek in Ref. [17], tack generally depends on the adhesive and face stock material. Based on theoretical considerations, one can assume that hot melts (with a lower-molecular-weight base polymer then solvent-based or water-based PSAs) and solvent-based PSAs (with soft base polymers and without low tack additives) yield better tack.

Tack and peel resistance are improved by tackification and plasticization [14,17,18,] (see also Section 8.2.1). Tackified polymers possess better tack, as do plasticized polymers. Because PSA bonding typically occurs at the plateau region of the viscoelastic curve, bonding (tack) is facilitated by lowering the G' (storage modulus) at this region (see also *Fundamentals of Pressure Sensitivity*, Chapter 6). G' can effectively be lowered by increasing the entanglement molecular weight of the polymer. PSA debonding happens at a much higher frequency when tack is improved by increasing the G'' (storage modulus) by increasing T_g. Peel resistance can be regulated by cross-linking as well [14] (see Section 8.2.2). The importance of specified regulation parameters of peel resistance (e.g., adhesive, coating weight, cross-linking, primer, and PSA geometry) for the main PSPs (labels, tapes, and protection films) was examined in Ref. [18] by Benedek, who demonstrated that for labels with a balanced adhesion–cohesion and high (normed) coating weight, cross-linking, primer, and adhesive geometry are the most important parameters to decisively modify peel, quite different manner from protection films, which require special adhesives as the main regulating parameter.

8.1.1.2.2 Formulation for Shear Resistance

Shear resistance was described in detail in Refs [17,18,25], in *Fundamentals of Pressure Sensitivity*, Chapter 8, and in *Applications of Pressure-Sensitive Products,* Chapter 8. Shear resistance is a function of adhesive nature; macromolecular characteristics, and the composite status of the PSA (see also Chapter 1), coating weight, face stock material, and adherent. As discussed in detail in Ref. [14], formulation for increased shear resistance is based on methods that improve the cohesion of the base adhesive raw material (e.g., by using hard monomers and high-molecular-weight polymers) or by formulation with cross-linking and filling (see Sections 8.2.2 and 8.2.3). For thermoplastic elastomers (TPEs) shear resistance strongly depends on tackification and tackifier characteristics [14,25] (see also Chapter 3). Reinforcing is principally achieved by fillers, by cross-linking, or through the use of associative tackifiers [14].

8.1.1.2.3 Formulation for Removability

Removability is related to energetic (rheologic) features and chemical adhesion. To ensure a low peel resistance, the external force must be balanced by the viscous and elastic deformation of the adhesive layer. In some cases, due to the self-deformation of the carrier material, reduced debonding energy is transferred to the adhesive–substrate interface (and adhesive–face stock interface), where low adhesion should allow an adhesive (contact) break (see also Chapter 1). In this situation, formulation for removability must allow energy absorbance (self-deformation) of the adhesive and low-level adhesion on the adherend surface. From the rheologic point of view, the distinct characteristics of

TABLE 8.3 Parameters of Removability

Parameters	How to Achieve Removability	
PSA-Related	Fundamentals	Practice
Polymer-Synthesis-Related		
Chemical composition	Low affinity	Nonpolar monomers, internal emulsifiers
Macromolecular characteristics	Low G' and G'', long plateau modulus	Molecular weight, M_e depolymerization–cross-linking, no oligomers
Formulation-Related		
"Softening" of PSA	Control of entanglement, modulus, T_g	External plasticizers
Cross-linked structure	Controlled flow, enenrgy dissipation	Cross-linking
Filled structure	Controlled flow, contact surface reduction	Filling
Detackifying	Controlled contact surface	Use of detackifiers
Tackifying	Improved anchorage	Low, selected tackifier level
Additive's level	No migration	Low surfactant level
Coating-Related		
Adhesive thickness–regulation	Controlled flow, controlled contact surface	Low coating weight
Adhesive image–regulation	Controlled contact surface	Patterned coating
Adhesive adherence–regulation	Controlled flow	Direct coating, primer, pretreatment
Carrier-Related		
Bulk properties of carrier	Controlled deformation, energy absorbtion, influence on coat-weight, influence on contact surface, peel angle	Choice of carrier material, stress history, geometry (thickness, shape) stiffness
Surface properties of carrier	Controlled flow	Anchorage

this type of adhesives are low bonding modulus, so the adhesive is very contact efficient, and low dissipation, which implies more elasticity or better removability (see also the application windows for removable PSAs in *Fundamentals of Pressure Sensitivity*, Chapter 6). Table 8.3 summarizes the parameters of removability.

The level of adhesion is characterized by peel resistance, which was discussed in our previous works [17,18]. Advances in this domain are described by Kim et al. in *Fundamentals of Pressure Sensitivity*, Chapter 7. Removability was discussed by Benedek in Ref. [18]. Because peel resistance is a function of the time–temperature dependence of the rheologic properties, removability also depends on stress rate. This means that, *ad absurdum,* each PSA can be considered removable using an adequate (i.e., very slow) debonding rate. Removability is a function of the application temperature as well. For instance, removable PSAs applied at room temperature and later exposed at low temperatures may behave as permanent adhesives due to the increase in cohesive strength. Some rheologic aspects of removability are described by Chang in *Fundamentals of*

Pressure Sensitivity, Chapter 5, as a function of the balance between the storage and loss modulus at various frequencies. From the point of view of macromolecular design, polymers for removable PSAs must have a low work of adhesion and a long plateau modulus over a wide frequency range, which ensures the same peel resistance and failure mode at various removal rates (see also *Fundamentals of Pressure Sensitivity*, Chapter 5). Low G' and G'' are required.

Repositionability and readherability can be considered special cases of removability. Repositionability and readherability are performance characteristics dependent on peel build-up. PSAs with high final peel resistance can also be used as repositionable products. For instance, a new adhesive with almost no tack and very high peel adhesion was described by Ko [26]. It is useful in hand applications requiring repositioning prior to full adhesion.

Repositionability and readherability allow the debonding of the PSP after its application on an adherend and its rebonding. Repositionability is an aging-related characteristic that requires a slow build-up of the adhesion on the substrate. In this case, peel build-up is delayed over time, but is not limited as an absolute value. Repositionable labels may also be permanent. Readhering labels are removable after application independent of the aging time, which means that their peel build-up is of limited value. Readhering requires balanced adhesive properties and excellent bonding characteristics. Therefore, the only manufacturing techniques that can be used for readherable products are those that do not influence the instantaneous tack of the adhesive. Repositionable and readherable products are required in those PSP classes where instantaneous tack provides product applicability.

The formulation-related manufacturing possibilities for removability are described in detail in Refs [13,27,28]. Off-line synthesis of raw materials (see Chapter 1) for removable adhesives is a decisive step in their manufacture. Low peel resistance is achieved by using harder monomers and avoiding monomers that might impart specific adhesion. High molecular weight and high cross-linking density also reduce peel strength. The energy dissipation (W) caused by the deformation of the adhesive as a function of the creep rate depends on the modulus of elasticity (E) of the adhesive, which depends on the molecular weight and cross-linking.

$$W = f(E) + f[v(t), dt] \tag{8.2}$$

Internal copolymerizable emulsifiers improve removability as well [28]. Incorporating ethoxylated amines into PSAs with carboxylic groups allows better control of peel. Formulating off-line synthesized, solvent-based acrylic polymers with detackifiers such as stearinic acid or polyalkylene oxides as detackifiers, and cross-linking agents (e.g., isocyanates and polyaziridines) leads to removable PSAs.

The most important parameters of the carrier, related to the removability of the PSA, are its flexibility and anchorage (adhesion) of the adhesive to the carrier. Adequate anchorage of the PSA on the carrier imparts good removability from the adherent. Anchorage is the phenomenon of adhesion between the face stock material and the adhesive. For fiber-forming, textured supports (e.g., paper), this is a physical phenomenon. Physical interaction and flow of the adhesive are the main components for anchorage of PSAs onto rough, textured surfaces. Removable, unformulated acrylic PSAs give

less anchorage on unprimed surfaces than tackified formulations. Anchorage is also a function of emulsifier level (see also Section 8.1.1.2.3); therefore, solvent-based acrylic PSAs give better anchorage than water-based ones. Untackified ethylene–vinyl acetate copolymer (EVAc) or carboxylated butadiene rubber (CSBR) exhibit poorer anchorage than acrylic PSAs. Tackification improves anchorage.

Peel depends not only on the deformability of the adhesive, but also on the flexibility and plasticity of the carrier. Energy dissipation during debonding depends on interfacial adhesion, which is a function of surface quality. In the case of removable adhesives, high-rate peel forces must be dampened by high energy dissipation (i.e., good anchorage of the adhesive on the face material is needed). Chalykh et al. [29] investigated the strength of PSA joints on different substrates. The strength of the adhesive bond for the substrate was ordered like the corresponding magnitudes of the thermodynamic work of adhesion. As noted by Müller and Knauss [30], peel energy (P_F) depends both on macroscopic factors of energy dissipation $f(R)$ and on the molecular factors of energy dissipation $g(M_c)$,

$$P_F = W_h \cdot g(M_c) \cdot f(R) \tag{8.3}$$

where W_h is the reversible work of adhesion. The adherence or anchorage may generally be improved using primers (see also Section 8.2). The influence of the carrier surface on removability was discussed in Ref. [8].

Adhesion depends on the contact surface; thus, some technical ways to achieve removability depend on formulation, whereas other modalities depend on the geometry of the adhesive layer; that is, they are (at least partially) a function of the coating technology. Contact surface reduction (the decrease in the ratio of contact surface to application surface of the adhesive) can be achieved by regulating the actual contact surface, the rheology of the PSA, and the chemical affinity between the adhesive and the substrate surface.

As discussed by Benedek in Refs [8,17], adhesive geometry (i.e., the form of the adhesive layer and its thickness) strongly influences peel resistance. Special coatings with discontinuous character of the adhesive layer exist, mostly to avoid the build-up of high peel resistance. The structure of the continuous adhesive layer also influences peel resistance. The coating device affects the shape of the adhesive layer (see also Chapter 10). For instance, cross-linked adhesives coated with gravure cylinder give peel values that differ from those obtained with a Meyer bar for the same coating weight (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Controlling adhesive flow to reduce the contact surface requires the build-up of an internal structure in the bulk adhesive. Such a structure does not allow rapid adhesive flow and penetration of PSA in the "rough" substrate surface; that is, it hinders the physical contact between the adhesive and adherend. The rheology of a highly viscous and partially elastic structure is regulated by means of cross-linking and filling (see Sections 8.2.2 and 8.2.3).

The same result is obtained by dividing the contact surface into small discrete areas (see Chapter 10). For nonadhesive contact sites, fillers were suggested. The contact surface of the adhesive is divided by formulation in an inhomogeneous adhesive mass, with

particles in the adhesive layer, that do not build up contact, because they are not adhesive, or not adhesive enough, or do not diffuse into the pores of the adherend. Such an adhesive layer can also be produced using inert filler particles that are placed on the contact surface. These particles are partially adhesive or elastic or "fully" adhesive, but too voluminous.

Contact hindrance for tape adhesives can be achieved using special fillers. For instance, a removable tape for paper contains PSA microparticles obtained from a cross-linked, milled PSA. The 50- to 100-μm particles are coated with 5 g/m^2. To reduce the contact surface and decrease build-up, elastic polymer particles with a diameter of 0.5–300 μm can be included in the adhesive as filler. To improve their detackifying effect, the particles may include an ionic low-tack monomer. Removable pressure-sensitive tapes containing resilient polymeric microspheres (20–66%) with a diameter of 10–125 μm, density of 0.01–0.04 g/cm^3, and shell thickness of 0.02 μm in an isooctyl acrylate–acrylic acid (IOA–AA) copolymer have been prepared as well.

The practice of pressure-sensitive design and formulation of solvent-based, water-based, and hot-melt PSAs (HMPSAs) for removability is described in Ref. [16]. For solvent-based removable formulations, cross-linked acrylics are generally used; for water-based removable PSAs, NR latex, styrene butadiene–latex, and plasticized or cross-linked acrylics are used. The tack of cross-linked compositions depends on the drying temperature. The nature of the tackifier resin affects the removability too. Less polar resins (e.g., hydrogenated methylester of rosin or glycerol ester of hydrogenated rosin) yield better removability. Detackifiers can be used as well (see Section 8.2.1.3). Removable hot-melt formulations are based on special elastomers [e.g., styrene block copolymers (SBCs) with high styrene content], multiblock styrene–butadiene–styrene (SBSs), or copolymers with a high-melting-point end-block, amorphous polypropylene (PP) and EVAc, together with special tackifiers (such as modified terpenes, aliphatic hydrocarbons, hydrogenated hydrocarbons, rosin ester, and low-molecular-weight hydrocarbons), plasticizers (e.g., naphthenic and saturated mineral oils), and detackifiers were suggested. Recent developments in acrylic block copolymers allowed the formulation of removable PSAs (see Chapter 3). Ref. [16] presents screening formulations for removable water-based PSAs, solvent-based PSAs, and HMPSAs.

8.1.2 End-Use-Related Formulation

The adhesive performance characteristics are the most important end-use properties of PSAs [17,18]. The choice of adhesive for labels (with the exception of the economical end environmental arguments) is determined mainly by adhesive properties (first by the value of peel resistance required for a given substrate). For tapes, the same criterion is valid. Unlike label suppliers, manufacturers of protective films offer the "same" products (with respect to standard peel value) with adhesives that are chemically or physically different; thus, their softness and dwell time on various substrates differ. Different rubber-based or acrylic-based adhesives are suggested for use on adherends with different roughness, which means that quite different adhesives (and applications) may exhibit the same peel value as a function of the substrate nature and application conditions (see *Applications of Pressure-Sensitive Products*, Chapter 4). In practice, for various

end uses the substrate nature and application conditions may differ as a function of the environment. Special PSPs are formulated for environmental resistance.

8.1.2.1 Formulation for Environmental/Chemical Resistance

Formulation for environmental resistance comprises resistance to chemical environment and to temperature. Formulation for environmental resistance includes the common formulation for storage resistance, that is, the design of an adhesive that displays anti-aging characteristics [15] (see also *Applications of Pressure-Sensitive Products*, Chapter 8) and the design of special compositions that impart water or solvent resistance [13,16] or solubility [16,31] to the adhesive (see also *Applications of Pressure-Sensitive Products*, Chapters 4 and 8). There are very different requirements concerning the storage and aging resistance of PSPs and their components. Storage and aging resistance include the stability of adhesive performance at room temperature and at application temperatures under a standard or special chemical environment. PSPs must be stable under well-defined storage conditions between 2 and 7 years. Detailed data regarding storage stability are given by Benedek in Ref. [13]. For dissolved or dispersed adhesives, thermal and aging stability comprise the rheologic stability of the dispersed system as well. A loss of stabilizer (due to hydrolysis, evaporation, or biological attack) affects their stability. For HMPSAs, thermal stability includes the stability of viscosity (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Generally, a formulation must provide antimicrobial resistance of the PSA as well. Coated, water-based PSAs must resist wet storage. Special recipes are required for pressure sensitivity at low application temperatures [13] and bond resistance at elevated temperatures [13,16,32] (see also Chapter 7 and *Applications of Pressure-Sensitive Products*, Chapter 4).

8.1.2.1.1 Formulation for Water Resistance/Solubility

As discussed in *Applications of Pressure-Sensitive Products*, Chapter 1, PSPs can be classified according to their water resistance. Water-resistant products are required for many applications [32]. Other (than adhesive) end-use requirements must also be taken into account for special labels (e.g., increased or decreased water sensitivity or mechanical resistance) [32]. For instance, carrier-free splicing tapes must also be water-soluble. The range of various PSPs with special water resistance is described in *Applications of Pressure-Sensitive Products,* Chapter 4.

Formulation for water resistance covers a wide range of resistance modalities and values of PSAs [32,33]. In this case we use the term "modality," because in some cases water resistance is well described by the resistance of the adhesive not to be solved in water (at very different contact or immersion times, temperatures, and pH values), but in other cases such resistance characterizes the first phases of a solution process only (i.e., water absorption; see *Applications of Pressure-Sensitive Products*, Chapter 1). Wet-surface adhesives must adhere on cold, condensed water-coated adherend surfaces. For several applications PSAs must resist atmospheric moisture, but be removable with warm water. Wine and champagne bottle labels must be removable in water without the supplementary addition of chemicals at 60°C (see also *Applications of Pressure-Sensitive Products*, Chapters 4 and 8). The test methods for water resistance/solubility are

described in *Applications of Pressure-Sensitive Products*, Chapter 8. PSPs with special water resistance can be imparted in water-resistant and water-soluble products. For special uses cross-linkable, water-soluble, and electrically conductive PSAs have been developed [31] (see also *Applications of Pressure-Sensitive Products*, Chapter 4). A new class of water-soluble and insoluble adhesive hydrogels, described by Feldstein et al. in Ref. [34], can be used in various pharmaceutical and consumer products. The fundamentals of this new class of PSAs were discussed in Ref. [6]. Hydrocolloid formulation based on the nanocomposite concept (general principles, morphology, rheology, antimicrobial use, and developments) were discussed by Kulichikhin et al. in Ref. [35]. The original nanocomposite concept consists of introducing a liquid crystal component with a cholesteric structure to a hydrocolloid formulation, as well as clay nanoparticles. In both cases nanospaces that can be used as traps for some active species appear in the formulation. Advances in hydrophilic adhesives are presented in Chapter 7.

Formulation for Water Resistance The water resistance of polymers depends on their polarity, crystallinity, and structure. The water resistance of dispersion-based coatings is primarily a function of their water-soluble additives (see also Section 8.2.4). Formulation possibilities for improved water resistance were described in detail by Benedek in Ref. [16]; they include the choice of adequate monomers for polymer synthesis, the right choice of physical state of the adhesive (100% solids or diluted and the dispersion characteristics of a water-based adhesive), the choice of technological additives (wetting agents, thickeners, fillers, etc.), and postcuring. Theoretically, for water-resistant applications, water-unsoluble, solvent-based adhesives should be used, but water-based acrylics that resist immersion in water have been synthesized as well.

Adhesives with excellent water resistance (humidity and condensed water resistance) are required for technical tapes and pressure-sensitive assembly parts in the automotive industry. This can be achieved with water-based raw materials (dispersions) using the tackifier's own surfactants. PSPs with improved water resistance are described in *Applications of Pressure-Sensitive Products*, Chapters 1 and 4.

Formulation for Water Solubility Formulation for water solubility was described in detail in Refs [13,16,31]. The formulating additives for water solubility are presented in Section 8.2.4. The range of special products with improved water solubility is described in *Applications of Pressure-Sensitive Products*, Chapters 1 and 4. Hydrophilic adhesives based on water-absorbing and amphiphilic polymers [e.g., polyvinyl ethers (PVEs), methacrylic polyelectrolytes] are described by Feldstein et al. in Chapter 7.

Water-soluble formulations may have a different raw material basis. They can be formulated with common, commercially available polymers or manufactured through the synthesis of special macromolecular compounds. Improvement in the water-absorbing capacity of hydrophobic PSAs by blending with hydrophilic absorbents is described by Feldstein et al. in Chapter 7.

For instance, according to information presented in Ref. [36], water-soluble adhesives for splicing tapes can be manufactured using polymer analogous reactions, polymerization, or polymerization and formulation. Their formulation depends on the degree of solubility required and on the adhesive-coating technology. For instance, water-releasable

labels and water-dispersible splicing tapes or medical tapes require different degrees of solubility. Building solubilizing functional monomers into a polymer or adding water-soluble agents to a formulation depends on the physical state of the adhesive. Emulsion copolymerization of certain water-soluble monomers is difficult because of their tendency to homopolymerize in water. Therefore, solution-polymerization is used. On the other hand, water-soluble additives (surfactants) can be fed into water-based dispersions without a problem. Screening formulations for water-soluble solvent-based, water-based, and HMPSAs are given by Benedek in Ref. [16]. The use of nontacky hydrophilic solubilizers in hydrophobic molten HMPSA requires special knowledge.

Both possibilities, that is, the formulation-based manufacture of water-soluble PSAs and their synthesis-based manufacture, are classic procedures. Formulation-based manufacture uses common PSAs that are solubilized through special additives or water-soluble polymers that are tackified. Manufacture based on common PSAs solubilized with additives was discussed many decades ago by Benedek [37,38]. The synthesis of water-soluble polymers was used first for protective coatings.

The choice of main elastomer and tackifying and solubilizing components depends on the required degree of hydrophilicity (i.e., water solubility, dispersibility, releaseability, etc.) and adhesive properties. Different water-resistance grades are required (see also *Applications of Pressure-Sensitive Products*, Chapter 8). It would be desirable to have a PSA that is tamperproof under ordinary-use conditions but that can be easily removed with water in a household or commercial cleaning process. Water-washable adhesives can be removed by immersion in cold or hot water. Fully recyclable, repulpable adhesives are needed also.

Special fully water-soluble labels were developed using a water-dispersible face stock material and a water-soluble adhesive. Water-soluble or water-activatable adhesives were formulated. In special cases (e.g., bottle labels, deep-freezer labels, medical tapes) common labeling adhesives need improved adhesion on wet surfaces (see also *Applications of Pressure-Sensitive Products*, Chapter 4). In this case the adhesive should work like a water-activatable composition. Water solubility needs a higher degree of hydrophilicity than water activatability. According to HyunSung et al. [39], the stickiness caused by common PSAs is the main obstacle in wastepaper recycling (i.e., repulping and paper making). Therefore, new PSAs must be developed that are repulpable in the papermaking process. The manufacturing technologies of repulpable PSAs can be divided into three categories: separable/removable, water-soluble and redispersible/recoverable (or screenable), and dispersible/soluble adhesives.

A few water-soluble polymers can be used for common water-soluble PSA formulations (e.g., vinyl pyrrolidone or vinyl ether homo- and copolymers). Water-soluble macromolecular compound vinyl pyrrolidone copolymers are used as the main component. For instance, a water-soluble pressure-sensitive hot melt is formulated with vinyl pyrrolidone–vinyl acetate (VAc) copolymers. The composition also includes a free monobasic saturated fatty acid with an acid number higher than 137. Water-soluble HMPSAs for labels are formulated with 35–60% vinyl pyrrolidone or VAc–vinyl pyrrolidone copolymer, together with free fatty acids. Fatty acids with 8 to 24 carbon atoms act as a solubilizer in a concentration of 3% or less; they can be formulated with vinyl pyrrolidone–VAc copolymers and water-soluble polyesters also. Water-dispersible

HMPSAs (i.e., recipes with less water solubility) can contain a classic elastomer component (e.g., 25–40% SIS), 25–40% tackifier, 25–10% fatty acid, and 25–10% poly(vinyl pyrrolidone) (PVP).

Although the use of PVP as the main water-soluble polymer, together with polyethylenoxides, was tested many decades ago, the intrinsic pressure sensitivity (for a well-defined ratio of components) was noted recently by Feldstein et al. [34], leading to a new range of plastomer-based PSAs and reinterpretation of pressure sensitivity [6,7]. As discussed by Feldstein and colleagues in Ref. [34] and in *Fundamentals of Pressure Sensitivity*, Chapter 10, PVP plasticized with glycols can also be formulated to yield pressure-sensitive hydrogels.

PVP-based formulations exhibit poor thermal stability. A hydroxyl-substituted organic compound (e.g., alcohols, hydroxyl-substituted waxes, polyalkylene oxide polymers) and a water-soluble *N*-acyl-substituted polyalkylene imine, obtained by polymerization of alkyl-substituted 2-oxazolines, can be used with better results as the main HMPSA component. Such water-releasable HMPSAs contain 20–40% polyalkylene imine, 15–40% tackifying agent, and 25–40% hydroxyl-substituted organic compound. For such recipes, water-soluble plasticizers whose molecular weight does not exceed 2,000 are preferred (e.g., polyethylene glycols of molecular weight of about 200–800). Fillers with increased organophilicity (e.g., fatty acid ester-coated mineral extenders like stearate/calcium carbonate compound) are suggested as well. Distearyl pentaerythritol diphosphite is used as an antioxidant.

Polyethyloxazoline has been proposed as a water-soluble base component for water-soluble hot melts. Formulations based on polyalkyloxazolines and water-insoluble polymers display (alkaline) water dispersibility, water activation, and solubility with alkalies, but they can also be used in water-soluble adhesive compositions. Water-dispersible hot melts are based on vinyl ester graft copolymers with water-soluble polyalkylene oxide polymers.

The repulpable recipe comprises an elastomer and a tackifier (as base PSA component), an AA copolymer to provide additional strength, and solubilizer components such as a polyalkylen imine, a functional diluent based on acid-functional polymeric compounds, hydroxyl-substituted organic compounds, and waxes. Such a formulation for repulpable general-purpose HMPSA can contain a thermoplastic polymer (20–50%), polyalkylen imine (10–30%), diluent (2–90%), wax (5–40%), tackifier (85–40%), plasticizer (0–40%), and filler. Vinyl polymers, polyesters, polyamides, polyethylene (PE), PP, and rubbery polymers prepared from monomers including ethylene, propylene, styrene, acrylonitrile, butadiene, isoprene, acrylates, VAc, functionalized acrylates, and polyurethanes (PURs) can be used as the thermoplastic component.

Ideally, both the main elastomer or viscoelastomer and the tackifier or plasticizer should be water soluble. In practice, such formulations are used for difficult applications like splicing tapes (see also *Applications of Pressure-Sensitive Products,* Chapter 4) or medical labels (see also *Applications of Pressure-Sensitive Products*, Chapter 4). For such applications, vinyl carboxy acid-based polymers, tackified with water-based resin dispersions, are used as well. A proposed formulation for water-soluble HMPSA comprises 22 pts ethylene–AA copolymer, 39 pts PVP, 11 pts plasticizer, 14 pts tackifier, and 14 pts polyethylene glycol (PEG), respectively. A simplified formulation contains 60 pts PVP, 30 pts PEG, and 10 pts phthalate plasticizer. By blending the PSA raw materials that have carboxyl groups with

reactive hydroxylamine and neutralizing the mixture, it is possible to regulate the solubility of the polymer. The synthesis of a special PSA on the basis of aminoalkyl methacrylates or methacrylamide derivatives leads to water-soluble polymers as well. Water-based PSA formulations that are removable with warm water contain 7–30% hydrophilic monomers. Formulating the water-soluble viscoelastic components with water-soluble resins yields better adhesivity and better water solubility. For instance, a water-activatable PSA containing a water-soluble tackifier (5–150% w/w) is described in Ref. [40]. Polyacrylates tackified with water-soluble PVE have been proposed [41]. Amine-containing water-soluble polymers and water-soluble plasticizers have also been proposed.

Water-soluble PSAs were polymerized by solution polymerization using 2-ethylhexyl acrylate (2-EHA), butyl acrylate (BA), VAc, and AA with varying AA contents [39]. The water-soluble PSAs were prepared with varying AA contents and blended with polypropylene glycole (PPG) with variation in its contents. With increasing AA contents in PSA, water solubility increased and also demonstrated good repulpability. The increased water solubility and repulpability indicate that these PSAs do not cause sticky problems in the paper-making process and also reduce production costs.

A special class of hydrophilic polymers was developed using the simultaneous plasticizing–cross-linking in PVP–PEG-based formulations [34]. Such compounds can be classified as water-soluble, super absorbents, medium absorbents, or weak absorbents. Hydrophilic adhesives are discussed in detail in Chapter 7.

8.1.2.1.2 Formulation for Chemical Resistance

Special label and tape applications require solvent resistance (see *Applications of Pressure-Sensitive Products*, Chapter 4). Generally, solvent resistance can be achieved by using cross-linked formulations (see also Section 8.2.2) or special raw materials. For instance, **s**olvent-resistant silicone PSAs were developed by Eckberg and Griswold [42]. They determined that tackifying *MQ* resins undergo a facile reaction with fluoroalkylsilanes to provide modified *MQ* resins compatible with fluorosilicone gums. Fluorinated silicone resin and fluorosilicone gums combine to make compositions with PSA properties similar to those of conventional silicone PSAs, with the added virtue of resisting solvent attack by hydrocarbon solvents. Noncoupled fluorosilicone PSA compositions have significantly improved solvent resistance but inferior peel adhesion as a function of the fluoro content of the fluorosilicone gum. Coupled fluorosilicone PSAs can be prepared with peel adhesion approaching that of conventional methyl silicone PSAs without sacrificing solvent resistance through proper selection of gum fluoro content and resin/gum (R/G) ratio. These new adhesives may be laminated to conventional silicone release liners to form pressure-sensitive constructions that can be readily packaged and dispensed.

8.1.2.1.3 Environmentally Friendly Formulation

In general, reduction or elimination of solvents from a technology constitute the main possibilities for environmentally friendly products. Replacement of toxic solvents, reduction of the solvent content, and recycling of the solvents (and other product components) offer other possibilities. Such changes in the manufacturing technology of PSAs and PSPs were discussed in detail by Benedek in Ref. [43]. The development of water-based PSAs and hot melts is a major contribution to environmentally friendly

products and product technology. The use of solvent-based acrylic PSAs has declined steadily for the past 10 years due to volatile organic compound (VOC) emission control regulation, such as the Environmental Protection Agency Clean Air Act, Title 5.

For instance, stemming from environmental concerns, developers and users of silicone PSAs have been seeking delivery systems that eliminate or minimize VOC content. Delivery systems under consideration generally fall into one of four categories: liquid solventless and high-solids PSAs applicable by traditional coating techniques, solventless and high-solids PSAs applicable by screen printing techniques, aqueous PSA emulsions, and HMPSA compositions. Each of these delivery system choices has ramifications for the range of composition materials that can be used, the final adhesive property profile obtained, and the processing equipment required. However, the benefits potentially reaped by the new delivery systems can be greater than solvent emission control alone [44]. It is to be noted that (due to the composite structure of water-based formulations, the narrow range of TPEs, and their limited aging resistance) this technological transfer leads to products with a lower environmental resistance. Differences in recyclability arise through formulation of water-based dispersions also. Protective colloid-based dispersions (e.g., EVAc) are processed more easily than surfactant-stabilized ones (AC).

Formulation for recycling includes the use of recyclable raw materials and their recycling technology. Recyclable raw materials comprise common materials and biodegradable products. Recycling of PSPs depends on the recyclability of product components, that is, of the PSA and the solid-state components (carrier and release liner) of PSP. These are so-called constructive components of the laminate. PSPs include technological product components as well; thus, recycling of PSA includes reuse of the dispersing medium (e.g., solvent or water) [45].

Recycling of carrier materials is related to recycling of paper and of plastic films. Both are affected by the recyclability of the PSA. Recyclability of paper supposes its nonadhesive status; that is, the paper carrier must be "cleaned" from the adhesive. There is a need to develop a technology that can process the "stickies" generated when materials containing PSAs are used in the manufacture of recycled fiber pulp [46]. Repulpability and its test were discussed by Czech in Ref. [31] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). In such repulpable systems the contaminants are not removed or separated, but their size is reduced through the use of mechanical forces and chemical agents. A better technical solution is given by the use of water-soluble PSAs (see Section 8.2.1 and *Applications of Pressure-Sensitive Products,* Chapter 4). A special method to assure the recyclability of tapes concerns their water solubility or dispersability. Both the adhesive and the carrier can be formulated as water-dispersible products. Fully water-soluble plastics can be used as raw materials for films also. For instance, a paper-based tape, recyclable as paper, is manufactured using a water-soluble adhesive based on alkali-soluble acrylic acid esters and PE or PP waxes and alkali-dispersible plasticizers.

Recyclability of plastic films as raw material for films requires high temperature resistance or compatibility of the coated adhesive layer with the polymeric film (e.g., rubber–resin adhesives) or its depolymerizability (e.g., acrylics). This procedure is used for rubber–resin adhesive-coated protection film only. Recyclability of polymer films was discussed, together with the manufacture of carrier films, in our previous work concerning developments on PSPs [43].

New European and German norms were introduced concerning the use of solvents and clean air [47]. The recovery of solvents used for solvent-based adhesives and printing inks is discussed in Ref. [20]. Absorption by active carbon and dissolution by steam, recovery by condensation, and afterburning were described comparatively. Polymerization and recovery of solvents for water-soluble acrylic PSAs was discussed by Czech in [31].

Environmental considerations imposed the development of plastics and adhesives with biodegradability. Such products were described in detail by Benedek in Ref. [20]. The recyclability and biodegradability of water-soluble PSAs used for water-soluble labels, splicing tapes, and operation tapes was discussed by Czech in Ref. [31] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Advances in medical products allowed the use of biocompatible and biodegradable (resorptive) PSPs as well (see *Applications of Pressure-Sensitive Products*, Chapter 4).

Changes in the materials of solid-state components and in the manufacturing technology of such components can lead to waste reduction. According to Tomuschat [48], glassine paper and PET are currently the standard materials for release liners in the roll-label industry. Owing to their high price, these materials are responsible for a major share of the overall costs of label stock material. Replacing paper with 30 μm biaxially oriented polypropylene (BOPP) and thermally cured silicone with ultraviolet (UV)-cured silicone (0.8 g/m^2), 135 μm global thickness is achieved, compared with standard label stock, where standard paper with 80 g/m^2 is coated with 20 g/m^2 PSA and combined with thermally siliconized (coating weight, 1.1 g/m^2) glassine liner (62 g/m^2). Such construction reduces waste up to 55%.

8.1.2.1.4 Formulation for Temperature Resistance

Various PSPs require high temperature and weathering resistance. For instance, weather resistance is required for advertising decals (see also *Applications of Pressure-Sensitive Products*, Chapter 4); "laser-resistant" adhesives for nameplates must exhibit enhanced temperature resistance (see also *Applications of Pressure-Sensitive Products*, Chapter 4). The standard temperature resistance of pressure-sensitive formulations is given by the rheologic characteristics of the components. As discussed in *Applications of Pressure-Sensitive Products*, Chapters 1 and 4, some special products must display improved temperature resistance (i.e., to beware their adhesive characteristics at extreme temperatures also). Such requirements include applicability at low temperatures (see *Applications of Pressure-Sensitive Products,* Chapters 1 and 4). where high modulus and wet substrate surface hinder adequate adhesive–substrate contact, and high temperatures, where the pronounced flow of the adhesive reduces its cohesion. Formulation possibilities for such temperature-resistant PSAs include the choice of an adequate base polymer and tackifying agent or the use of special technological additives.

Formulation for Low-Temperature Use Formulation for low-temperature use is required mainly for freezer tapes and labels (see *Applications of Pressure-Sensitive Products*, Chapter 4). Formulation for such products was described in detail in detail in Refs [13,16,43]. Screening formulations for deep-freezer PSAs for labels and tapes are given in Ref. [16]. The main general-purpose PSAs are formulated for maximum tack at 38–40°F. Low-temperature applications require low storage modulus. For adhesives for common

labels a storage modulus value of $10^{4.5}$ Pa (at 20°C) is required. For PSAs on deep-freezer labels a lower modulus value, 10^4 Pa (at 20°C) is suggested. PSAs for low-temperature applications include soft formulations with lower-molecular-weight polymers and with plasticizers. Generally, common deep-freezer adhesives are based on rubber solutions (with a minimum application temperature of −10°C) or acrylic dispersions (with a minimum application temperature of −10°C). Although no tackifiers are suggested for deep-freezer labels because at low temperature tackifiers become nontacky fillers, low-softening-point (10–85°C) resins can be used. Classic formulations for low-temperature applications use NR (50–75 pts), SBR (with 12% styrene), regenerated rubber (3–8 pts), and PVE (1–3%). Polyterpene resin 1–4% (SP 115°C), rosin ester (1–3%), and carboxylated alkylphenol resin (2–15%) are suggested as tackifiers. Such (with isocyanate) cross-linked formulations can be used between −29 and +113°C. For low-temperature applications CSBR with high (80%) butadiene content or SBCs with high diblock polymers are also preferred. For such applications acrylics are suggested. UV-light-curable, prepolymer-based acrylics are suitable for deep-freezer or removable applications as a function of the UV dose. Screening formulations for rubber–resin-based and acrylic-based deep-freezer formulations are given by Benedek in Ref. [16].

Formulation for High-Temperature Use Formulation for high-temperature use was described in detail in Ref. [16]. It uses base polymers with increased thermal resistance (see Chapter 6). High-temperature resistance may be obtained with highly cohesive elastomers containing self-cross-linking units, with high-softening-point tackifiers or cross-linking agents and fillers. Generally, cross-linking and filling also improve temperature resistance. A special case of formulation for improved temperature resistance is given by SBCs. In their range, styrene–ethylene–butene (SEBs) copolymers possess higher temperature resistance than conventional styrene–isoprene–styrene (SIS). The well-known technique to increase the temperature resistance of SBCs is the use of end-block reinforcing resins. For instance, for styrene–butadiene multiblock copolymers, high-melting-point styrene-associating resins improve temperature resistance. Aromatic resins (e.g., coumarone–indene resin, styrene resin) impart good thermal resistance. A high level (75%) of coumarone–indene resin (SP 145°C) increases the T_g of the polystyrene (Pst) domain from 100 to 120°C [14]. High-temperature-resistant formulation is generally required for special tapes (e.g., automotive, construction, insulation, and masking tapes) [13,43] (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

8.1.2.1.5 Formulation for Time/Temperature Resistance

PSAs must display storage resistance; that is, they must beware their end-use characteristics for a long time. Aging resistance includes the stability of material characteristics during static and dynamic storage, handling, and application of the product [16]. Formulation for aging resistance is described in a detailed manner in Refs [15,45]. The antioxidants and UV-light-protecting agents used to improve weathering, thermal and light resistance, their classes, and working mechanism are described. The main antioxidants (commercial name, chemical composition, and supplier) and their suggested use (polymers to be stabilized and level of stabilizer) are presented [46] (see also Section 8.1.4.1.1).

8.1.2.2 Formulation for Other End-Use Performances

As discussed in detail in *Applications of Pressure-Sensitive Products,* Chapters 1 and 4, PSPs can be classified according to their main function, as well as their application domain. Starting from the same raw materials, formulation for labels, tapes, or protective films can be quite different according to their end use. Such formulation must take into account the special requirements for a given function (e.g., flame resistance, conductivity, etc.), tailored for each segment of the application domain and the economical considerations. As discussed by Benedek in Ref. [32], the product surface influences the label end use as well as the product form; the product surface affects the tape and protection film application. The product to be labeled, taped, or protected influences the application methods of PSPs and their formulation.

8.1.2.2.1 Formulation for Special End-Use Characteristics

Formulation for special end-use characteristics can impart flame resistance, electrical conductivity, antimicrobial function, Food and Drug Administration (FDA)/BGA-required properties, etc. Formulation for flame resistance was described in detail by Benedek in Ref. [15]. Formulation for conductivity was also discussed in Ref. [15]. The electrical characteristics (e.g., antistatic performance–surface resistivity and electrical conductivity) of PSPs were discussed by Benedek in Ref. [9]. Conductive fillers (discrete and web-like) and filling methods for PSPs were described by Benedek in Ref. [46]. Current conductive tape adhesives contain glass spheres coated with silver (33% silver) or silver and copper (18%) and possess specific surface conductivity of 10^{-5} to 10^{-11}(G) [49].

Bioelectrodes cover a special domain of PSPs with electrical conductivity. Their main representatives, such as the transcutaneous electrical nerve simulation electrode, the electrosurgical unit electrode, the electrocardiogram electrode, the defibrillator pad, and the bio-feedback electrode, are described by Czech in Ref. [31]. Taking into account the increasing importance of this domain, electrical conductivity of PSAs is discussed in detail in *Applications of Pressure-Sensitive Products*, Chapter 2. Antimicrobial function of special hydrocolloids was discussed by Kulichikhin et al. in Ref. [35] (see also *Applications of Pressure-Sensitive Products,* Chapter 4). Another special application field of PSAs includes food contact. Pressure-sensitive labels are also applied directly to foods, such as fruits and vegetables. FDA 175.125, Part (b), applies to this category (Pressure-Sensitives, Raw Fruits, and Vegetables). For adhesives with indirect contact with food, 21CFR 171.1 (b), with the list of additives, must be fulfilled. Current European regulation 1935/2004 is valid for materials intended to come into contact with foodstuffs [50]. The European Framework Regulation 1935/2004 states general guidelines that also apply for adhesives, printing inks, or lacquers. For the first time, a manufacturer in Europe could be prosecuted for the influence of packaging on foodstuffs. In Germany, the Foodstuffs and Consumer Goods Code (*Lebensmittel und Futtermittel Gesetzbuch*) of 1 September 2005 is valid [51].

8.1.2.2.2 Application Domain-Related Formulation

Products that display special, end-use-related performance characteristics (see above) include PSAs with different formulation according to the application domain. For

instance, a splicing tape (see *Applications of Pressure-Sensitive Products*, Chapter 4) must possess water solubility, which differs from that of a bottle label (see also *Applications of Pressure-Sensitive Products*, Chapter 4) or of a medical product (see *Applications of Pressure-Sensitive Products*, Chapter 4). The electrical conductivity of an automotive tape (see *Applications of Pressure-Sensitive Products*, Chapter 4) or of an electronic tape (see *Applications of Pressure-Sensitive Products*, Chapter 4) differs from that of a medical tape (see *Applications of Pressure-Sensitive Products*, Chapter 4).

8.1.2.2.3 Economic Considerations-Related Formulation

Economic considerations affect the formulation of PSAs as well [13]. The main economic parameters of the manufacture of PSPs include the cost of raw materials, the manufacturing equipment, and the productivity of the manufacturing equipment. The costs of raw materials fluctuates as a function of the global market and the developments in the synthesis or availability of raw materials. The relative costs of a raw material class compared to another can vary also. The costs for processing of vehicle-free or low-pollution formulations are lower than the costs for solvent-based recipes. On the other hand, the physical status of the adhesive influences the productivity of the coating equipment. HM-, solvent-based, or water-based PSA coating and drying or cooling technology offers different productivity and cost level for a given PSP. The relative costs of equipment and manufacturing procedures, as well as performance, are affected mainly by technical development. The adhesive-related costs are influenced by commercial and political strategy. However, in practice there are only a few products with "fully" interchangeable formulations, and the choice of a recipe or a manufacturing technology is decisively affected by the available equipment. Material costs and productivity-related considerations impose inexpensive manufacturing technologies with 100% solids. In-line coating of multiple layers and simultaneous laminating substantially improve productivity. HMPSAs can be laminated instantaneously with the release liner; that is, in-line adhesive coating and siliconizing are possible. Productivity-related formulation was discussed by Benedek in Ref. [13]. The choice of the main components of an adhesive recipe (e.g., base elastomer or viscoelastomer and tackifier) is also important. As noted in Ref. [15], concerning the costs for equipment and energy consumption, HMPSAs offer the most economical solution; unfortunately, their raw materials are more expensive than those for solvent-based and water-based PSAs. The global production costs (material and technology) are about 100% for solvent-based adhesives and hot melts and 120% for water-based PSAs. Economic consideration-related formulation was discussed in detail by Benedek in Refs [13,15].

8.1.3 Product Construction-Related Formulation

The solid-state components of a PSO (e.g., the carrier material and the release liner) and the construction of the pressure-sensitive laminate influence the formulation of the PSA too. The influence of the solid-state components of the laminate and its composite structure on the rheology of PSAs and PSPs was evaluated by Benedek in Ref. [8]. The product build-up-related design and formulation was described in Refs [13,52]. As discussed in Chapter 1, the composite structure of the PSP decisively affects PSA formulation.

8.1.3.1 Carrier-Related Formulation

Principally, the chemical composition of the carrier material (e.g., paper, plastic film, metal) and its bulk and surface properties (continuous film, fabric, woven/nonwoven, porous/closed, etc.) affect the coatability of the adhesive and the convertibility of the PSP. Wettability of the carrier, its chemical and thermal sensitivity, its porosity and composite structure, its polarity, and its geometry influence coatability, the anchorage of adhesive, laminating, confectioning, and end-use properties (see also Figure 8.1). As discussed in Chapter 1, common PSPs have a construction that possesses an upper critical coating weight and carrier thickness (see Figure 8.2).

The manufacture of carrier material for PSPs was described by Benedek in a previous book [43]; the general and special requirements for paper used as carrier material (for labels, tapes, protective webs, and release liner), the general and special requirements for synthetic films used as carrier material (for labels, tapes, protective webs, and release liner), and other carrier materials (e.g., foams, nonwovens) were discussed. In Ref. [18], the influence of surface properties and bulk properties of the carrier material on the adhesive properties and regulation of the adhesive properties with the carrier were investigated. Carrier-dependent formulation was described in Ref. [13]. A separate discussion of formulation for the main PSPs (labels, tapes, protection films, etc.) as a function of the carrier (paper, film, etc.) is given in Refs [13,16]. The carrier material can impose direct or transfer coating. As noted in Ref. [53], the chemical basis of PSA formulations for direct or transfer coating is quite different (see also Chapter 10).

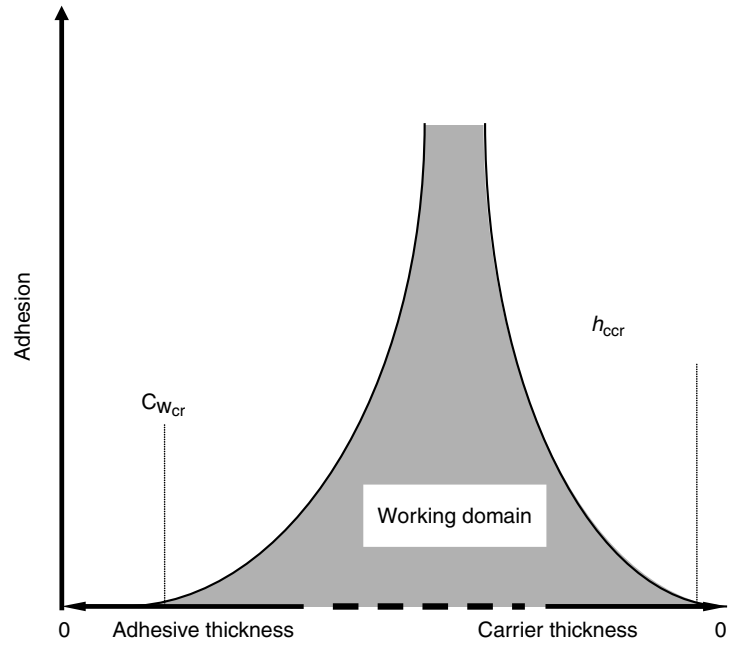


FIGURE 8.2 The working domain of PSP, delimited by critical adhesive-coating weight (C_{wcr}) and critical carrier thickness (h_{ccr}).

The carrier material can impose the use of precoating (see Chapter 10) or pretreatment (see Chapter 10). Adhesive migration and penetration (see *Applications of Pressure-Sensitive Products*, Chapter 8) depends on both the carrier and the PSA. For instance, for some specific applications in which oil may migrate into the face stock film or the bonding substrate, polar plasticizers such as phthalate, dibenzonate, and dimer acid are the choices for HMPSAs (see also Chapter 3). The anchorage of the adhesive is a function of the carrier as well. Therefore, various carrier materials impose different adhesive formulations (see *Applications of Pressure-Sensitive Products*, Chapter 1).

8.1.3.2 Release Liner-Related Formulation

Generally, the chemical composition of the release material and the PSA influences the release force and, thus, the converting and application properties and technology of the PSPs. Different abhesives are used for the main classes of PSPs; silicones are preferred for labels and special tapes, and carbamates, fluorinated derivatives, etc., are used for protective webs and special tapes [43,46]. Owing to the release liner- and adhesive-dependent debonding (i.e., peel force on the release liner) and the possible mutual interaction of the adhesive and release liner, formulation must take into account the type (e.g., silicone/nonsilicone, solvent-based, water-based or solventless, thermal or radiation-cured) grade of the release material. Transfer coating uses the release liner as a carrier [20,40] (see also Chapter 10); therefore, its surface characteristics are decisive for wettability of the adhesive and for the optical properties of the PSP (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Developments in silicone release materials and their influence on PSA technology are discussed in detail in Chapter 9.

8.1.3.3 Pressure-Sensitive Product Build-Up-Related Formulation

Construction of special pressure-sensitive laminates (e.g., multilayer labels, forms, tapes, or carrierless PSPs such as transfer tapes) impose the use of various adhesives with a sophisticated formulation. For instance, pressure-sensitive tapes filled with glass microbubbles have a foam-like appearance and character and are useful for purposes that previously required a foam-backed PSA tape. Foam-backed adhesive tapes are commonly used to adhere an article to a substrate, but such filled foam-like PSAs are suggested for removability also [28]. Glass microbubbles (at least 5% by volume) are embedded in a polymeric matrix with a coating thickness of 0.2 mm.

8.1.4 Raw Material-Related Formulation

Although the development of macromolecular chemistry allowed the synthesis of new rubber-like products (elastomers) and viscous components (resins), their number is limited, especially in the range of melt-processible elastomers (the raw materials for hot melts) and for water-based materials. Thus, formulation modalities depend on raw materials and differ according to the available raw material basis. Although, theoretically, both main formulation variances for pressure-sensitive adhesives (i.e., the rubber–resin-based recipe and the viscoelastomer-based recipe) are available as 100% solids or dispersed systems (dispersions or solutions), in practice there are preferred

formulations for each raw material class. Certain raw materials can, in principle, be used for different formulations (100% solids or dispersed systems); however, their chemical and macromolecular characteristics limit their preferred use for certain formulations. For instance, tackifiers work best with base polymers with a glass transition temperature below 0°C (see also Section 8.2). Because VAc polymers have a higher T_g, they do not work with tackifiers (see also Chapter 6). Polymers with built-in viscoelasticity offer a broader chemical basis for the manufacture of the whole range of adhesives (i.e., HM-, radiation-cured, solvent-based, or water-based PSAs). Generally, the choice of a raw material class determines the range of possible performances. For instance, butyl tapes, tested in comparison with acrylics for bonding exterior trim mouldings to automobiles, perform better at low temperature and pass cold shock tests; this behavior is due to the low T_g of the butyl system (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Soft rubber–resin PSAs better fulfill the deep-drawing requirements (lubrication) for protection films than acrylics. This is due to the more elastic network of NR (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Raw material-dependent formulation was described by Benedek in Refs [15,43]. Elastomer-based formulation including NR, synthetic elastomers with random sequence distribution, hydrocarbon-based block copolymers (SIS and SBS copolymers, saturated block copolymers, branched copolymers, sequenced copolymers, acrylate-based block copolymers, synthetic hetero block copolymers) were described in detail by Benedek in Ref. [14]. Viscoelastomer-based formulation, including solvent-based, water-based, and hot-melt acrylics, VAc copolymers, PVEs, and PURs were also discussed. The main raw material classes used for PSAs are presented in Chapters 1 through 8.

8.1.4.1 Formulation of Dispersed/Solved Adhesive

The manufacture of PSPs by coating imposes the use of a fluid-like adhesive. Such a PSA is supplied as a solvent-based or water-based adhesive. The first radiation-curable adhesives, based on oligomers and reactive diluents, can be considered solvent-based systems. A comparison among solvent-based, water-based, and HMPSAs is given in Ref. [45].

8.1.4.1.1 Formulation of Solvent-Based Adhesives

As discussed in detail in Refs [13,16,45,53], solvent-based PSAs have a broader raw material basis. They can be formulated as tackified elastomers, acrylics, PURs, PVEs, and other materials. Their formulation can be either the manufacture of an adhesive (e.g., rubber–resin PSA) or the modification of an adhesive (e.g., AC, PUR, PVE). Solvent-based acrylics are recommended for durable mounting tapes, outdoor PSPs, medical tapes, protective tapes, and high performance decals [16] (see also *Applications of Pressure-Sensitive Products*, Chapter 4). They offer the unique possibility of various cross-linking modalities [14,54], with or without a previous mechanochemical destruction of the base polymer [14] and, thus, their adhesive and end-use properties (especially their tack, shear resistance, and removability) are easy controlled (see also Section 8.2.2).

In the first stage of development NR–resin-based formulations were used as solvent-based adhesives for tapes and labels; later, synthetic rubbers were introduced. Screening formulations for rubber–resin solutions are listed by Benedek in Ref. [16]. Cross-linking

of solvent-based formulations has been used since the beginning of PSA technology. Solvent-based cross-linked formulations were developed for each product class (see *Applications of Pressure-Sensitive Products*, Chapter 4) due to their relatively broad raw material basis and easy regulation of their cross-linking degree by the aid of raw materials and manufacturing conditions (see Chapters 1 and 10). First, NR was used and, later, synthetic elastomers were processed. Each requires special technology. Formulation of NR includes different procedures to improve the adhesive, cohesive, and aging characteristics. Tackification, cross-linking, filling, and stabilizing are needed. It should be stressed that NR has excellent formulability; it can be depolymerized, detackified, re-polymerized by cross-linking, and tackified with high polymers, tackifiers, or plasticizers. Tackification of NR is the classic way to obtain PSAs. NR can be used together with polar elastomers and reactive resins (phenolic resins) to achieve temperature and solvent resistance. The reaction is carried out by mastication of the components. Generally, such solvent-based cross-linked formulations require special drying conditions to achieve the simultaneous drying and cross-linking of the adhesive (see Chapter 10).

Synthetic rubber-based PSA formulations were developed as solvent-based, water-based, and 100% solids recipes. The best known synthetic elastomers used for solvent-based PSAs are the styrene–diene copolymers; BR, polyisobutene (PIB), acrylnitryl–diene copolymers, halogenated diene–diene copolymers, silicones, PURs, etc., were used as well (see also Chapters 2 through 8). Styrene–butadiene polymers used in the adhesive tape industry contain a gel, either a microgel or a macrogel. A microgel is built into the polymer during synthesis by cross-linking between polymer chains within the latex particle. A macrogel results from cross-linking between particles, which builds up large masses of polymer, generally due to instability in the polymer. Macrogel formation can be prevented by improving rubber stability. Although a stable viscosity could be achieved through proper selection of solvent/resin/rubber level and total solids, the characteristics of the elastomer are the major determining factor in viscosity stability.

Advances in macromolecular chemistry have enabled regulation of the viscoelastic character of macromolecular compounds. In principle, such viscoelastic raw materials can be used as base elastomers and tackifying viscous components. Acrylics, VAc copolymers, silicones, and PURs are the most important viscoelastomers. With the exception of VAc copolymers, they are used mainly for solvent-based formulations (see also Table 8.5). Tackification and cross-linking are the main formulating modalities for viscoelastomers. Formulation practice of solvent-based adhesives was described by Benedek in Ref. [16]. Their cross-linking was discussed in detail by Czech in Ref. [54].

8.1.4.1.2 Formulation of Water-Based Adhesives

Solvent-free, water-based, and 100% solids adhesives are being used more and more to meet the toxic products emission acts. The replacement of solvent-based adhesives with water-based ones has been a continuing trend in the industry for reasons of air quality, safety, and economics.

Water-based PSAs can be formulated as rubber–resin- or viscoelastomer-based recipes. In the range of synthetic elastomers, styrene–butadiene copolymers are the most used raw materials. Their formulability depends on chemical composition and molecular weight. Their chemical composition is characterized by the level of styrene and polar

comonomers. Their molecular weight is described by the assembly of linear and cross-linked polymer chains. For instance, soft and tacky butadiene–styrene latices possess 30% styrene. As discussed in *Fundamentals of Pressure Sensitivity,* Chapter 1, such dispersions have a composite structure, characterized by gel content. Gel build-up has been noted in acrylic dispersions too.

For water-based PSAs, formulation is mostly a modification of the base adhesive (AC, EVAc, PVE, etc.), but it is also focused on the adhesive and converting properties. In this case, the modification of the base adhesive is more complex because of its built-in (bulk) chemical composition and its dispersed system-related chemical composition (particles with a composite structure); therefore, formulation affects the dispersion stability as well.

For water-based dispersions the chemical basis of the main polymer influences the technology used for its dispersing and, thus, the chemical and dispersion properties of the product. As a consequence, the formulation is affected too. For instance, VAc polymers and copolymers with an acid pH yield acid dispersions that must be formulated in the acid domain. Therefore, in this case nonionic tackifiers should be used. On the other hand, chloroprene latices must be neutralized. In this case, the choice of neutralizing agent requires special know-how.

For dispersed systems formulation also depends on the storage time. Dispersing quality affects the static shelf-life of the dispersion and its shear (machining) stability. In some cases dispersing affects the adhesive properties of the PSA. For instance, when water-based viscoelastic and viscous components are mixed (e.g., acrylics with tackifiers), peel resistance increases with storage time of the mixture (up to a limit). Water-based formulation was described by Benedek in Refs [16,41]. Formulation of water-based adhesives must include formulation for processibility; that is, it uses special technological additives. Generally, the special additives (e.g., surface active agents) included in the formulation of water-based adhesives (during synthesis and formulation) negatively affect their adhesive and end-use performances. Therefore, the choice of water-based formulations for special adhesives is limited. For instance, as noted by Lin et al. [44], although aqueous PSA emulsion is a commercially important delivery system for organic PSAs, it is not widely used for silicone PSAs. The use of surfactants is required for silicone PSA emulsions, which leads to numerous performance implications caused by the presence of trapped surfactants in the finished PSA tapes.

Recent advances in this field are presented by Foreman in Chapter 5. A special case of water-based formulations and chemistry and manufacture of hydrogels was discussed by Feldstein in Refs [12,33] (see also Chapter 7 and *Applications of Pressure-Sensitive Products*, Chapter 6).

8.1.4.2 Formulation of 100% Solids Adhesives

Adhesives without a dispersing medium include hot melts and (partially) radiation-curable compositions. Hot melts are based mainly on off-line synthesized thermoplastic elastomers (see Chapter 3) and radiation-curable compositions that use oligomers and macromers as the base raw material for in-line synthesis (see Chapter 1).

HMPSAs possess some major deficiencies: excessive thermoplasticity, poor UV resistance, and limited plasticizer tolerance. Their applicability is limited by the restricted formulating freedom for removable recipes. The sealing tape industry relied heavily

on HMPSAs based on SBCs because they offer a good balance of shear, tack, and peel resistance at a reasonable price. Developments in acrylic HMPSAs offer new formulation possibilities for medical PSAs (see Chapter 3).

In-line synthesis of radiation-curable PSAs and PSPs by polymerization (initiation of photopolymerization, monomers, comparison of UV/electron beam (EB)-induced polymerization, hybrid systems, and EB curing) and macromerization (raw materials for macromerization and acrylates for macromerization) were described in detail by Benedek in Ref. [14]. Radiation curing was also discussed Ref. [14]. UV-light-induced cross-linking was described in Ref. [31]. Techniques of UV polymerization of PSAs (use of thickened monomer mixtures and prepolymerized monomer mixtures) and UV cross-linking (based on UV cross-linkable acrylic PSAs and UV cross-linkable HMPSAs) were described by Do and Kim in Ref. [55]. Photo cross-linking of solvent-based acrylic PSAs (UV-light sources and photoinitiators) was described by Czech in Ref. [54] (see also Section 8.2).

8.1.4.2.1 Formulation of Hot Melts

Hot melts have been used for labels, tapes, and decals since the early 1970s. Their formulation was discussed in detail in Refs [13,16,25]. Natural and thermoplastic rubbers provide a relatively nonexpensive raw material basis for HMPSAs. Hot-melt coating assures the highest coating speed (see Chapter 10) and consumes only 25% as much energy as a solution-based coating process. Therefore, several tapes are formulated with HMPSAs (see *Applications of Pressure-Sensitive Products*, Chapter 4). On the other hand, the adhesive properties of HMPSA formulations are strongly affected by the narrow range of available TPEs. Although linear and branched products with unsaturated or saturated mid-blocks were developed, and the regulation of the diblock triblock sequence distribution provides new possibilities for controlling the elastomer network, the main adhesive characteristics of such formulations are determined by the temperature limits of the segregation driven by physical forces and by the compatibility of the whole TPE (which is nontacky) or its domains with solid-state or liquid tackifiers. As noted in Ref. [13], in a different manner from tackified NR, where the elastomer network exists even after its "diluting" and the temperature does not influence its rigidity significantly, in tackified TPEs pronounced viscous flow can always appear under chemical and thermal attack.

Styrene–diene block copolymers used for HMPSAs (common products and multiblock copolymers) were described in detail in Refs [15,46,53]. Common synthesis methods were discussed in Refs [15,25]; special manufacturing procedures were presented by Benedek in Ref. [15]. Advances in synthesis and formulation of HMPSAs are discussed by Hu and Paul in Chapter 3.

Single-component HMPSAs were developed as well. The proper selection of comonomers and synthesis additives led to the development of olefinic copolymers that are PSAs when unformulated. Acrylic phase-separated block copolymers were manufactured also [15] (see Chapter 3). However, the most common TPEs must be formulated. The shear modulus, G', of a PSA at ambient temperature ranges typically between 10^3 and 10^6 Pa, and the glass transition temperature (T_g) of a PSA is typically below 10°C [56,57], or 30 to 70°C lower than the application temperature. As a result, the properties of neat SBCs are not suitable for most PSA applications. SBCs inherently have a T_g that is too low and a G' that is too high at room temperature. Viscoelastic processes cannot be activated if

the T_g is too far from the application temperature. Furthermore, the adhesive cannot deform and wet the surface if it is too stiff. As a consequence, SBCs must be formulated with tackifying resins and plasticizers to achieve the desired properties (see Chapter 3).

Formulation of synthetic, hydrocarbon-based block copolymers (SIS, SBS, saturated block copolymers, branched copolymers, sequenced copolymers, etc.) was discussed by Benedek in Ref. [14]. Other block copolymers (acrylics, silicones, PURs, propylene copolymers, and polyesters) were presented by Benedek in Ref. [46]. Special hot-melt-based formulations (e.g., removable, water-soluble, etc.) were presented by Benedek in Ref. [16]. Advances in block copolymer-based hot-melt adhesives are described in detail in Chapter 3 by Hu and Paul. Tackifiers used for the formulation of SBCs were discussed in our previous works by Benedek [15,46] and Parks [25]. Recent advances in this field are discussed by Hu and Paul in Chapter 3.

Because of the complex equipment and know-how required for HMPSA formulation (in a different manner from water-based PSA formulation), special suppliers of ready-to-use HMPSA should be preferred.

8.1.4.2.2 Formulation for Radiation-Curable Systems

The base raw materials for radiation-curable systems are described in Chapter 1. Radiation-induced curing was discussed in detail in our previous works [14,53]; the monomers, oligomers, initiators, and tackifiers were presented. UV-curable PSAs were discussed in detail by Do and Kim in Ref. [55] and by Czech in Refs [28,54]. Tackification for postcuring was discussed by Benedek in Ref. [14]. Radiation-curable 100% solids, based on acrylics, are used as radiation-cured "warm melts" (see also Table 1.3 in Chapter 1). Such materials are generally low-viscosity prepolymers that must be post-cured. For instance, an HMPSA on an acrylic basis, synthesized by solution polymerization, can be coated at 90 to 140°C and is cross-linked using EB and UV or chemical cross-linking (by NCO-containing systems).

8.1.5 Technology-Related Formulation

As discussed in detail by Benedek in Ref. [13], pressure-sensitive design and formulation influence the global manufacturing technology and the global product technology (i.e., product application). In this context, formulation is related to equipment, productivity, and environmental considerations. Formulation affects the choice of adhesive manufacturing and processing technology, coatability, drying, and running speed. It influences the converting properties related to dimensional stability (characterized by shrinkage, lay flat, and migration) and the confectioning properties.

The formulation recipe and the formulation technology depend on the raw materials used. Both the manufacture technology of the PSA and the coating technology of the adhesive may differ according to the raw materials used. Formulation must ensure the processibility of the adhesive raw materials, the adhesive, and the PSP also (see Chapter 10). The PSA layer can be coated on the carrier material as a dispersant-free, 100% solids material or as a liquid composite with a dispersed or solved adhesive in organic solvents or water. Because of the different abilities of the raw materials to be coated in molten or dispersed status, their formulations also vary. The adhesive raw

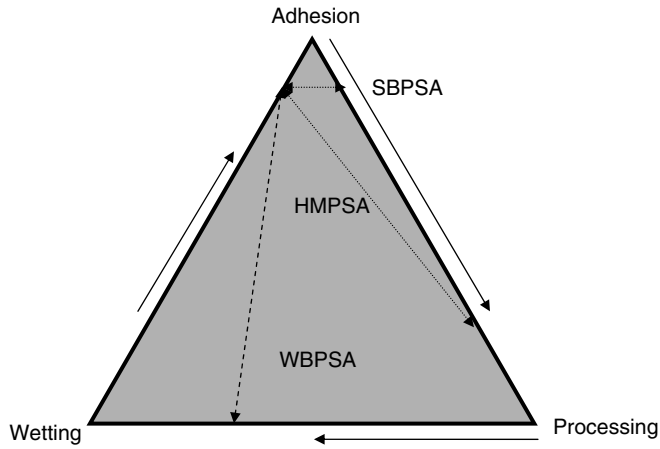


FIGURE 8.3 The scope of formulation as a function of the physical state of the adhesive.

materials must be mixed (see Chapter 10) and transformed in a fluid coating-component, which must be coated and transformed into a solid-state layer. The fluid adhesive must be processible with a given coating device. For instance, hot melts are manufactured by mixing the elastomeric and viscous components. This process requires special equipment as a function of the base components of the recipe [15] (see also Chapter 10). The adhesive produced must also be tailored with respect to processibility; that is, it must have a given viscosity at a given processing temperature and temperature stability. In this case, the choice of main components influences their miscibility and mixing ability, and the choice of the tackifier resin influences the viscosity of the molten polymer, but plasticizer and oils are also necessary for regulation. Owing to their high viscosity, HMPSAs are easily applied as a wettable liquid layer; for low-viscosity adhesives, formulation for coatabiliy is more difficult. The scope of formulation (i.e., its required influence on the adhesive or technological properties of the PSA) depends on the physical state of the adhesives. As illustrated in Figure 8.3, hot melts are formulated to achieve pressure sensitivity and, to be processible, water-based adhesives are formulated for adhesion and coating performances. Solvent-based PSAs are formulated mainly for adhesion control.

The various technology-related product characteristics are tested according to methods described in *Applications of Pressure-Sensitive Products*, Chapter 8. Their correlation with adhesive flow (rheology) as the main rheologic characteristic is presented in Table 8.4, which demonstrates, unfortunately, that the chemical composition and composite structure of the PSA alone play only a secondary role in their conversion properties. Other factors, such as the solid-state components and processing technology, are more important concerning the conversion parameters of PSPs. Thus, PSA formulation must be completed with adequate PSP construction and manufacturing technology.

8.1.5.1 Formulation for Coating

The formulation for coating (i.e., coatability) was described by Benedek in Refs [13,43]. As discussed in detail in Ref. [13], formulations may differ according to coating technology.

TABLE 8.4 Effects of Adhesive Flow

Flow in Laminate Cross-Direction (Vertically)		Flow in Laminating Direction (Horizontally)	
Performance	First Effect	Performance	First Effect
Adhesive properties		Adhesive properties	
Peel resistance	PSA anchorage	Shear resistance	Creep
	Dwell time	—	—
Removability	Residue	—	—
Shear resistance	Creep	—	—
Converting properties			
Printability	Migration	Printability	Shrinkage (curl, lay-flat)
	Shrinkage	Cuttability	Bleeding
Cuttability	Stiffness	—	—
	Telescoping	—	—

Origin of Cross-Directional PSA Flow			Origin of Machine-Directional PSA Flow		
Carrier	PSA	Processing Technology	Carrier	PSA	Processing Technology
Porosity Chemical composition	Rheology (G′/G″) Composite structure (additives, humidity)	Laminating pressure Unwinding tension Drying conditions	Smoothness Processing (built-in tensions)	Rheology Composite structure	Laminating pressure Unwinding tension

Depending on the physical status of the coatable adhesive, formulation for coating is the manufacture of the adhesive (e.g., hot melts) or its modification only (e.g., water-based acrylics). Therefore, the physical status of the adhesive and its rheologic characteristics affect the coating technology and the coating devices used. Vice versa, the coating technology and the particular coating device used require a certain viscosity and solids content and influence the formulation (see Chapter 10).

Hot melts or extrusion-coated thermoplastic adhesive layers are applied in a molten state. HMPSAs contain lower-molecular-weight raw materials and a high level of micromolecular components (except new acrylic block copolymer-based formulations; see also Chapter 3). The adhesives may further contain up to 25% by weight of a plasticizing or extending oil to control wetting and viscosity [16,25,45]. The molecular weight, chemical composition, and macromolecular characteristics of the base elastomer and of the tackifying components affect the coating viscosity. For instance, SBS-based formulations demonstrate much higher viscosities than SIS-based recipes. Formulations based on SEBs and a high-melting point-hydrocarbon resin have high viscosity. The styrene content of the SBC affects the tack, holding power, and viscosity (see Figure 8.4). The sequence distribution and the sequence length influence the viscosity of SBCs as well. For instance, a pure triblock copolymer possesses higher viscosity than a blend of di- and triblock copolymers.

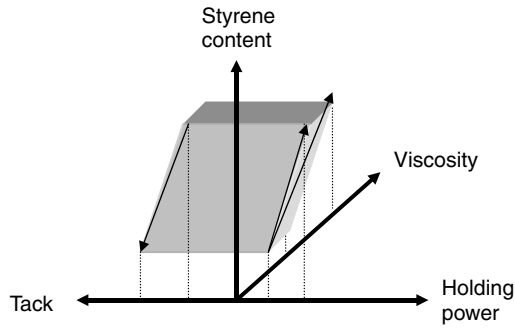


FIGURE 8.4 The influence of the styrene content on the adhesive and processing properties of SBCs.

With a 100% solids content, radiation-curable PSAs can also be coated (at room or elevated temperature) in a liquid state. The viscosity of radiation-curable, macromer-based products is much higher than the viscosity of common, solvent-based adhesives, but significantly lower than that of common HMPSAs. The medium viscosity of the prepolymer makes it easy to apply to the support.

Fluid, water-, or solvent-based formulations may have various rheologic characteristics, which impose the use of a well-defined coating method or vice versa; that is, the existent coating device imposes adaptation of the formulation to its parameters (see Chapter 10). Various coating devices can process adhesives that differ in viscosity and foam generation. For instance, formulation required for a Meyer rod differs from a recipe to be coated with a reverse-roll coater. An adhesive for rotogravure has a viscosity of 75–100 mPa · s and foaming of 2–5% in comparison with adhesives for a Meyer rod (with a viscosity of 300–800 mPa · s and foam generation of 10–20%) and an adhesive for knife-over roll (with a viscosity of 4000–8000 mPa · s and foam generation of 10–30%).

As discussed in detail by Benedek in Ref. [45], coating technology is a function of the chemical composition of the adhesive, the physical status of the adhesive, the product class, and the product build-up. In practice, the coating properties are the result of the coating performance characteristics of the coated mass (adhesive, abhesive, lacquer, printing ink, etc.) of the solid-state components to be coated (face stock or release liner) and of the coating technology. Unfortunately, the coater can regulate only the latter ones.

The coating technology depends on the carrier material as well. Generally, coating of plastics is more difficult in comparison to paper because of the lack of porosity and the nonpolar surface. The maximum running speed is lower for films in comparison with paper. Cratering, adhesive-free places, and coating weight differences are the main defects of a coated adhesive layer. Wetting-out of plastic films depends on temperature, vapor saturation of the atmosphere, and electric charges on the surface. Hot-melt formulation for films should take into account the temperature sensitivity of the carrier material. In some cases the adhesive is coated on the release liner (transfer coating). In this case, the coating properties of the liner carrier, as well as those of the abhesive-coated release liner, are important.

Most coating quality problems can be avoided by using a web pretreatment (see Chapter 10) or precoating (priming). The formulation of primers will be described, together with the priming technology, in Chapter 10.

In certain classic tape manufacturing procedures (used for plasters), a soft, solvent-free adhesive is calendered onto or into a fiber-like, fabric material (roll-press coating). In such cases the penetration of the adhesive ensures its anchorage. (Penetration as an adhesion-improving factor should be taken into account in the manufacture of removable products through the choice of direct coating; see also Chapter 10 and Table 8.3.)

Generally, formulation for coatability includes formulation for wetting-out, machining performances, running speed, and drying.

8.1.5.1.1 Formulation for Wetting-Out

The coating technology must ensure coating of the PSA on the solid-state carrier material (face stock or liner) as a continuous, smooth adhesive layer with adequate anchorage (bonding force). In adhesive coating the manufacturer has the potential to regulate the coating properties by proper formulation of the adhesive, by the choice of the carrier material, by the use of a primer, and by the choice of coating device or coating technology. Current PSP manufacture uses low-viscosity adhesives that are coated on (generally) nonporous, carrier materials at high running speed. In this case, coating of the PSA on the carrier material depends on the rheology of the liquid adhesive (dispersed/dissolved or molten), the characteristics of the carrier material, and the coating technology. For a given coating technology, the coating properties depend on the rheology of the adhesive and the surface characteristics of the carrier material. For a dispersed or dissolved adhesive, the coating properties depend on the components of the dispersed system and its wetting characteristics. Wetting-out is a function of the surface tension of the carrier material and of the surface tension and rheology of the adhesive [8]. In Ref. [8], the rheology of water based-dispersions was examined in comparison with the rheology of solvent-based PSAs. Common acrylic PSAs need more wetting agents for transfer coating than for direct coating. The theoretical basis of wetting-out, static/dynamic wet-out, and the role of surface tension and viscosity in wetting were examined. The driving force for dynamic wetting is, in fact, the surface tension of the adhesive rather than the work of adhesion [58]. Thus, the wet-out of water-based systems constitutes a difficult problem because of the high surface tension of water, the low viscosity of the most important ready-to-use formulations, the low density, and the transfer technology used for coating. The most important key issues concerning the wet-out are wet-out as the combination of wetting/dewetting; dynamic versus static wetting; factors acting against dewetting; parameters influencing wetting/dewetting (surface tension, contact angle, viscosity, and density); surface tension and parameters influencing it; contact angle and the problems of measuring this parameter; and the influence of viscosity (versatility, wet-out, coating weight).

The surface of the solid-state carrier material influences coating through its texture (structure), porosity, surface tension, and chemical affinity. Chemical affinity ensures the anchorage of many solvent-based adhesives on plastic films or of functionalized

(carboxylated) latices on paper. It is the reason for precoating a carrier with a reactive (e.g., polyisocyanates, reactive resin, etc.) primer. Chemical affinity is also a factor in the regulation of the bonding force of polar self-adhesive films (see *Applications of Pressure-Sensitive Products*, Chapter 7).

Surface treatment of the carrier (see Chapter 10) and appropriate choice of the surface-active agents for a formulation (see Section 8.2.4) allow control of dynamic wetting-out (see also *Applications of Pressure-Sensitive Products*, Chapter 8).

Coating rheology must lead to a wettable, stable, running time-independent liquid layer with a smooth surface after drying under applied shear forces. The rheologic behavior of polymer solutions is a result of solute/solvent interaction; it depends on the properties of dissolved PSAs and the solvent system. The coating rheology of solvent-based PSAs is the rheology of a true solution; thus, it is mainly viscosity driven and simpler than that of water-based systems. Synthetic raw materials for solvent-based adhesives are homogeneous, whereas natural raw materials are not. In general, rubber–resin adhesives display a broader variation of the solution properties than acrylic based adhesives.

In coating solvent-based adhesives, highly viscous, low-surface-tension liquids are used; therefore, in this case wetting-out is easily controlled. The use of special solvents or solvent mixtures constitutes an additional possibility for surface tension control of solvent-based adhesives. Generally, solvents used for solvent-based PSAs have a low surface tension (25–30 mN/m) in comparison to that of water (72 mN/m) or even of aqueous dispersions (35–42 mN/m). Here, the main problem is related to the chemical sensitivity of many plastic carrier materials to organic solvents. Another special problem is the change in viscosity of cross-linked systems.

Of the technological properties of dispersed adhesive systems, wetting ability is the most critical performance characteristic for coating. The real wetting/dewetting behavior of a latex cannot be approximated in the laboratory because of shearing of the dispersion on the coating (metering) roll, which improves wetting, and the competition between dewetting and drying imposed coalescence. Shear on the coating machine depends on its construction, as does foaming. Shear contributes to good wetting; foaming can be avoided with the use of defoamers, so it works against wet-out. Unlike solvent-based adhesives, formulating only has a limited influence on the coating rheology of water-based adhesives. Key parameters include adhesive build-up on the machine and mechanical stability due to insufficient flow, coagulum build-up on the machine and during formulation (mechanical stability), coating uniformity (stripped, textured structures, insufficient flow), stability of the viscosity (thixotropy and decrease of the viscosity, either reversible or irreversible), and foam formation. Tackification strongly influences the wettability of water-based formulations. The wetting ability of various aqueous tackifier dispersions is presented in Ref. [45].

The coating versatility of HMPSAs is limited; generally, special agents (e.g., waxes, oils) are used in formulation to extend the coatability range of the adhesive. The viscosity of current HMPSAs is of an order of magnitude higher than that of solvent-based PSAs and even higher than that of water-based PSAs. As discussed by Benedek in Ref. [14], in this case the choice of the base elastomer, its styrene content, is decisive for viscosity regulation.

8.1.5.1.2 Formulation for Machining Performances

Machining performances include the parameters that allow high-speed processing of the PSA and web, leading to a perfect product. As discussed previously, the quality of the coated liquid adhesive layer depends mainly on the formulation for coating, that is, on wetting-out, but other quality parameters must be examined too. These are well known from the processing of other (non-pressure-sensitive, web-like) finishes. A variety of water-based products, such as cold-sealing adhesives, adhesives for lamination, primers, and finishing coats, are routinely used in film conversion. Blisters, grit, ribbing, haze, and foam are always found with such products. During the coating process, disturbing phenomena may occur, such as adhesive build-up on the machine, coagulum build-up on the machine and in the coated layer, turbulence in the coated adhesive layer, and changes in viscosity and foam formation.

The minimum viscosity to be used depends on the surface tension. In practice, the coating weight depends on several parameters such as viscosity, running speed, and solids content. Viscosity is a function of solids content; on the other hand, it influences coating speed. As noted in Ref. [8], the interdependence of the coating parameters (running speed, solids content, and viscosity) is not linear. Running speed is a function of the drying ability of the PSA. The influence of the formulation on the running speed was examined by Benedek in Ref. [13]. The most important parameters of a liquid solvent-based adhesive can be easily and precisely adjusted because the (mechanical) stability of the system is independent of viscosity (or solids content). The coating speed of solvent-based adhesives is their most important converting property and there is no limit (minimum speed) on the coating speed because of the unlimited wet-out of these adhesives [59].

Drying is a complex phenomenon depending on the physical and chemical characteristics of the adhesive. Such physical characteristics include the parameters of the dispersed/solved system. For solvent-based adhesives, the quality of the dry coating depends on the evaporation rate of the solvent, which is a function of the coating thickness, solids content, solvent characteristics, and drying conditions. Another feature is the sensitivity of the coated adhesive layer to the drying speed (rate of diffusion of solvents used). The dependence of the drying speed on coating weight was discussed by Benedek in Ref. [17]. The influence of PSA design and formulation on drying was described in Ref. [13].

For common water-based dispersions, the upper limit of the running speed is given by the maximum drying speed; for high-solids dispersions it is the maximum speed leading to a smooth coated layer, and for medium-viscosity dispersions it is the maximum speed that limits foam formation. As discussed in Refs [14,45], drying speed of water-based PSAs is affected by tackification and plasticizing.

8.1.5.1.3 Formulation for Postcoating Reactions

Special formulation is required for PSAs polymerized or cured by radiation (by EB, UV-light, or mixed techniques). Such formulations are based on monomers (see Chapter 1), oligomers (see Chapter 1), or polymers (see Section 8.2.2.). Postcoating modification of the adhesive (i.e., its polymerization or cross-linking) is carried out as a finishing process of the PSA supplied by off-line synthesis (see Chapter 1), generally by thermal or radiation-induced cross-linking (see Chapter 10). Postcoating synthesis is carried out by

radiation-induced reactions. In this case, formulation must take into account the radiation absorbance of the base formulation components and the choice of adequate initiators.

8.1.5.2 Formulation for Web Converting

Web converting covers various coating and confectioning operations that transform the web-like, adhesive-coated laminate into a finite web-like product (e.g., protective web, tape, etc.) or a discrete PSP (e.g., label, form, etc.). Converting is discussed in Chapter 10. For such operations, special laminate performance characteristics are required (see *Applications of Pressure-Sensitive Products*, Chapter 8). Formulation for converting properties was described by Benedek in Ref. [13], taking into account the influence of the formulation on the parameters of dimensional stability (i.e., shrinkage, lay flat, and migration). Shrinkage and lay flat were discussed in detail by Benedek in Refs [60,61] as printing-related performance characteristics of the carrier material. As noted, the main components of the "pure" carrier-shrinkage (i.e., without PSA) include the manufacturing-induced component, the environmental component, and the coating-related component. The test of dimensional stability was discussed by Benedek in Ref. [32] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Another problem is migration, which is affected mainly by the adhesive. Migration resistance of various PSAs was examined by Benedek in Ref. [17]. Tackified acrylic PSAs demonstrate better migration resistance than competitive raw materials.

$$\text{Migration: AC (Tackified)} > \text{EVAc (Tackified)} > \text{CSBR (Tackified)} \tag{8.4}$$

8.1.5.2.1 Formulation for Mechanical Web Processing (Confectioning)

Mechanical web processing is the so-called confectioning, the process that uses cutting, slitting, die-cutting, etc., to manufacture a finite PSP from the continuous, web-like laminate. Such operations require that the pressure-sensitive laminate behave like a whole, and no disintegration of the pressure-sensitive composite occurs. This requirement can be fulfilled by the right choice of laminate components and manufacturing technology. Generally, during handling and processing web telescoping or smearing may appear. Both phenomena depend on the adhesive and its formulation (see also *Applications of Pressure-Sensitive Products*, Chapter 8).

Winding is one of the most used operations during laminating and web processing. For common tapes, slitting and winding are the last finishing operations (see also Chapter 10). Winding/unwinding are principally energetically characterized mechanical operations. The unwinding resistance influences the confectioning versatility of the tape and its ease of application. Different unwinding behavior is to be expected for a tape based on a hard acrylic or a soft HMPSA.

For labels, cutting and die-cutting are the main converting operations. For solvent-based acrylic PSAs there are no problems with cutting and slitting, but die-cuttability is not optimal for solvent-based rubber–resin adhesives because of the elastic character of the adhesive. An advantage of water-based PSAs is their better die-cutting and guillotine cutting, although tackified formulations can cause die-cutting and slitting problems. For SBCs, confectioning properties strongly depend on sequence distribution [13].

Die-cutting is related to matrix stripping. Therefore, the release properties affect the die-cutting properties. Formulation influences adhesion on the release liner [59].

Cuttability and its dependence on the adhesion–cohesion balance of the adhesive, on the chemistry and rheology of the PSA, adhesive properties (tack, peel resistance, and hot-shear resistance), coating weight, anchorage of the adhesive, laminate thickness and stiffness, and product build-up were described and evaluated quantitatively by Benedek in Refs [59,61]. The influence of tackification on cuttability is discussed by Benedek in Ref. [45]. The influence of the carrier material on the die-cuttability (e.g., film thickness and bow-up ratio) was examined in Ref. [59]. The influence of the release liner on cuttability was evaluated as well. As noted, both the liquid component of the laminate and the solid components (face stock and release liner) affect cuttability. Theoretically, low-tack, high-cohesion PSAs and isotropic, nonelastic, high-density carrier materials improve cuttability. In practice, low-tack, low-elasticity, and high-cohesion PSAs display better cuttability. There is no direct correlation between the cohesion of the adhesive tested as shear resistance and cuttability. Filled, strongly cross-linked PSAs (i.e., nonviscous and nonelastic) compact structures offer the best cuttability.

8.1.5.2.2 Formulation for Web Postcoating

Postcoating of the pressure-sensitive laminate includes operations such as postlaminating, lacquering, or printing (see Chapter 10). To improve the adhesive performances of the PSA layer or the surface characteristics of the carrier material, other nonadhesive or abhesive coatings can also be applied, such as printing inks and antistatic agents (see the following).

8.1.5.2.3 Formulation for Web Handling

Formulation for web handling ensures web transfer during the various manufacturing steps. Rolldown properties of tapes are very important. Such characteristics depend on the release properties of the back of the carrier. Friction and autoadhesion during web transfer or storage may cause blocking. Blocking occurs in sheet-like products as well as in reel-like products. To avoid bonding of adjacent (contacting) plastic surfaces, antiblocking agents are used. Blocking causes the unwinding resistance of tapes or solid-state tape components. Tapes with an olefinic carrier material are noisy. If unrolling is carried out at high speed, as in the operation of cutting the spool for rolls with semiautomatic and automatic machines (see also Chapter 10), a high noise level is encountered. The noise level is likely related to the mechanical properties and surface characteristics of the carrier material, the adhesive/abhesive performances, and unrolling conditions. Improving the surface tension (i.e., increasing it to more than 33 mN/m) reduces the noise level. Modification of the adhesive by addition of a mineral oil causes a substantial reduction of the noise level upon unwinding the tape. Further improvement can be achieved using a release coat or special treatment of the carrier back. Polyvinyl carbamate, polyvinyl behenate, etc., can be used as a release layer in this case. It should be mentioned that in some cases blocking and sealability are required performances for a carrier material; for such special applications, blocking may be required. For instance, the use of heat-sealable face stock allows the manufacture of "single material type pocket labels."

8.1.5.3 Formulation for Product-Application Technology

Formulation must take into account the product application technology. As discussed in *Applications of Pressure-Sensitive Products*, Chapter 4, application technology is determined by product class. For instance, labeling properties depend on label adhesion to the release liner (i.e., on the release or peel force). The actual application conditions affect formulation within the same product class. However, the large variance in products and their application technology in each class require various adhesive formulations. Different application (labeling) technologies are used for small labels and decals, machine (gun) labeling, and hand-applied labeling [17] (see also *Applications of Pressure-Sensitive Products*, Chapter 4). In most cases, the adhesive tack and release force (peel force from the release liner) must be closely monitored. Reel labels require an aggressive tack, whereas sheet labels require more cohesion and less tack. Therefore, the base elastomer for reel/sheet labels will be selected in a different manner. Cohesive, low-tack, high-molecular-weight polymers of short (side)-chain acrylics, and EVAc are adequate for such sheet applications. Soft, very tacky polymers of EHA or BA (i.e., long side-chain acrylics) are preferred for reel labels. These may be used as solvent-based or water-based adhesives. Competitive formulations for reel labels may also be designed on a HMPSA basis (see also Chapter 3). Water-based formulations are high-tack, tackified acrylics or CSBR-based, tackified PSAs. The use of special ethylene vinyl acetate maleinate multipolymers was also suggested. The first-generation ethylene vinyl acetate–dioctyl maleate copolymers offered good tack and peel strength, broader specific adhesion than acrylates, and excellent polyvinyl chloride (PVC) plasticizer resistance. Cohesive strength remains limited, however, and the product is used mainly in roll-label applications at moderate to high service temperatures.

Generally, the water-based adhesives for labels are tackified formulations with a resin level above 30% w/w (paper labels). This is required by their high-speed, low-pressure application on difficult adherent surfaces.

8.2 Formulation Methods

As noted by Benedek in Ref. [13], in industrial practice formulation is the blending of different components of a recipe to achieve adequate technological and end-use performance characteristics. Principally, formulation for end-use properties, based on mixing components, includes tackification and cohesion regulation as the main procedures [14]. The adhesive properties can be improved by tackification with other viscoelastic components, resins, and plasticizers (see Section 8.2.1.) or by formulation with special (reactive and nonreactive) additives that allow modification of cohesion (see Sections 8.2.2 and 8.2.3) or of technological performance characteristics (see Sections 8.2.3 and 8.2.4). A general compatibility exists between various acrylic PSAs, as well as between acrylic PSAs and other polymers. However, no similar compounding freedom exists for rubber- or EVAc-based polymers (see also Chapters 3 and 5). Formulation for adhesive properties and for technology is correlated. For instance, formulation of HMPSAs with the aid of viscous components allows tackifying (regulation of tack and peel), removability, and easy processing.

8.2.1 Tackification

Tackification, as discussed in Refs [18,43,45], has been used to improve the adhesive properties of PSAs, that is, the performance of adhesive-coated PSPs. As noted by Benedek in Ref. [18], regulating the adhesive properties includes regulating the adhesive properties with the adhesive per se and regulating the adhesive properties of PSPs with the adhesive structure and geometry (see also Table 8.3). Such regulation covers the control of the chemical composition of the adhesive by tackification, softening, and cross-linking of the adhesive. For the whole range of PSPs, tackification is more than modification of the adhesive; it also involves the carrier [52] (see also *Applications of Pressure-Sensitive Products*, Chapter 7) and other coating components (e.g., ink or primer) (see Figure 8.5). As discussed by Benedek in Ref. [14], the physical state of the adhesive strongly influences the scope of tackification. For solvent-based adhesives, tackification is carried out to improve the adhesive properties, for water-based adhesives to improve the adhesive and wetting and coating properties, and for HMPSAs to improve coatability and adhesive properties.

Principally, tackification is the formulation made to improve tack and peel resistance. In some cases (e.g., SBCs, silicones, or plastics-based hydrogels), no tack exists without tackification. For instance, neither the silicone polymer nor the *MQ* resin exhibits adhesive characteristics. Yet a mixture of silicone polymer and *MQ* resin in an appropriate ratio exhibits rather fascinating adhesive properties.

According to Ref. [14], tackification can impart various tack grades (i.e., dry or wet, temporary or permanent); that is, it can improve the common tack on dry substrate surfaces or the special tack on wet surfaces. The improved tack can be constant in time (as is generally) or disappear (e.g., for so-called semipermanent PSAs based on crystallizable polyolefins or polychloroprene). Concerning the site of tackification, it can act on the whole polymer or on preferred segments of this polymer (see Figure 8.6).

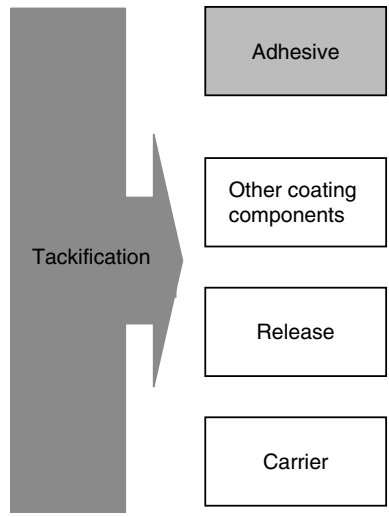


FIGURE 8.5 Use of tackification for self-adhesive products.

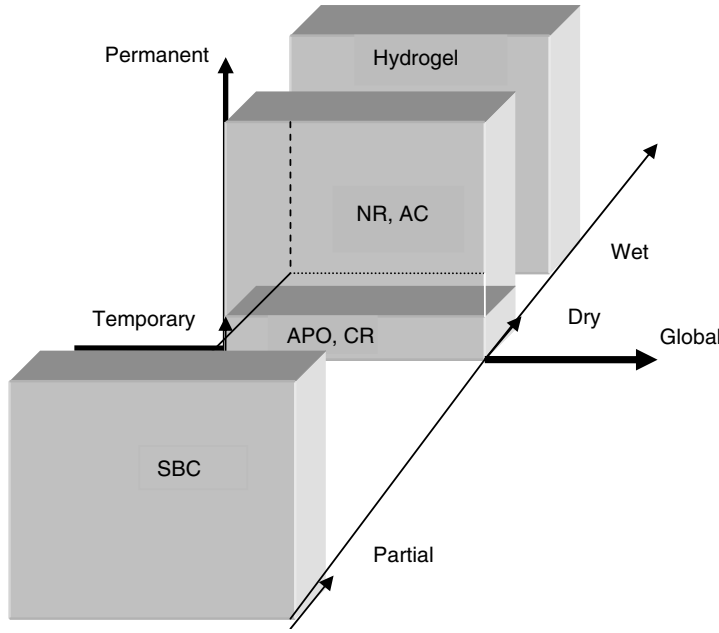


FIGURE 8.6 Tack and tackification grades as a function of PSA raw materials.

For instance, NR or acrylates are tackified as a whole (global tackification). SBCs are tackified preferentially on the mid-block or on the end-blocks (partial tackification). Tackification of both reduces segregation. Dry/wet tackification is discussed in detail by Benedek in Ref. [14]; the role of surfactants and water-soluble polymers in this process is also described. Tackification of polyolefin-based, so-called semipermanent PSAs has a temporary effect only. Crystallization (like for chloroprene-based products) can cause loss of tack. A special case of tackification is the formulation of pressure-sensitive hydrogels, which can act as bioadhesives. As noted in Ref. [12], within the framework of classic adhesive science, bioadhesion can be defined as a pressure-sensitive character of adhesion toward highly hydrated soft surfaces composed of mucin (see also Chapter 6). In contrast to bioadhesives, conventional PSAs are mainly hydrophobic. The distinctive feature of bioadhesives is a plasticizing effect of water. The new hydrogels were discussed in Refs [7,33] and in Chapter 7.

Tackification of the adhesive requires mutual compatibility [43,60] (see also *Fundamentals of Pressure Sensitivity*, Chapters 3, 10, and 11). For compatible adhesive components (most rubber–resin systems), an acceptable estimate of the tan δ peak temperature can be made using Fox's equation (this is important for the "application windows"; see also *Fundamentals of Pressure Sensitivity*, Chapter 5). As discussed by Benedek in Ref. [43], compatibility, reactivity, solubility, melting point, and absorptivity are the main technical criteria for usability of tackifier resins. Noncompatibility is taken into account by the tackification of adhesives with a composite, segregated structure (i.e., SBCs) only (see also Chapter 3) or by tackification of the carrier (see *Applications of Pressure-Sensitive Products*, Chapter 7). Tackification of the adhesive requires full or

TABLE 8.5 Tackification Modalities

	Tackifying Additive			
PSA Raw Material			Viscous Component	
Elastomer	Elastomer	Viscoelastomer	Resin	Plasticizer
Natural rubber	Masticated NR	PVE	Resin	Plasticizer
SBR	—	PVE	Resin	—
CSBR	Low-molecular-weight NR	PVE	Resin	Plasticizer
	Low-molecular-weight CSBR	—	—	—
SBC	Diblock SBC	—	Resin	Plasticizer
	Low styrene content SBC	—	—	—
Butyl rubber	PIB	PIB	—	PIB
Viscoelastomer				
Acrylics	—	Acrylics, PVE PVE	Resin	Plasticizer
PVE	—	PVE	—	—

partial compatibility; tackification of the carrier (see *Applications of Pressure-Sensitive Products*, Chapter 7) requires compatibility or noncompatibility.

Generally, the goal of tackification is to improve tack and peel resistance or removability. This may be quantified by knowing the base performance of the adhesive and the chemical or macromolecular characteristics of the formulating components. Tackification can be related to the viscoelastic parameters of the polymer. Supposing that tack is bonding related, to improve it the adhesive must be softened and its modulus (the elastic component) must be reduced. Therefore, theoretically, each additive that softens the adhesive, that is, reduces the plateau modulus, works like a tackifier. This means that, depending on the viscoelastic characteristics of the base polymer, a wide range of various compounds (e.g., elastomers, viscoelastomers, resins, plasticizers) can work as plasticizers (see Table 8.5).

The side effects of tackification (i.e., formulation made to improve tack) cover the adhesive, coating, converting, and end-use properties of the PSAs and PSPs (see Table 8.6).

Tackification depends on the main polymer to be formulated [14]. For elastomers, tackification is decisive, because it transforms the elastomer in a viscoelastomer with pressure sensitivity. For viscoelastomers, tackification is only a method to improve tack and peel. As discussed by Benedek in Ref. [14], tackification can be carried out with elastomers, viscoelastomers, viscous polymers, and plastomers.

Chemically different elastomers or elastomers with different macromolecular characteristics can be blended as tackifiers with the base elastomer. For instance, NR–latex improves the shear resistance of CSBR and its low-molecular-weight grades improve tack. On the other hand, addition of SBCs to NR improves cohesion. Soft CSBR dispersions can be blended with hard ones. Formulations based on polyalphaolefins demonstrate cohesion break and need another rubber; therefore, SIS and SEBs are added at a level of 3–7%, and at such level they are compatible. A special case of formulation with high polymers is mixing polymers with the same chemical composition, but different

TABLE 8.6 Side Effects of Tackification

Positive Effect on		Negative Effect on	
Adhesive properties	Notes		Notes
Tack	—	Shear resistance	Except certain SBC-based formulation
Peel resistance	Limited effect		
		Removability	Except plasticizing
Coating properties			
Viscosity	For hot melts	Shear stability	For water-based PSAs
		Increase of radiation dosage	For UV-cured formulations
Conversion properties	No positive effect	Cuttability	—
		Migration	—
		Bleeding	—
		Shrinkage	—
		Telescoping	—
End-use properties			
Temperature resistance	For certain SBC formulations	Water resistance	—
		Low temperature application	—
		Biocompatibility	—

macromolecular characteristics [e.g., molecular weight, molecular weight distribution (MWD), or sequence distribution]. In the case of SBCs, the nature of the mid-block, the styrene content, the molecular weight, and the sequence length and distribution are the main regulating parameters of the adhesion–cohesion balance (see also Chapter 3).

Tackification by mixing of viscoelastic components is illustrated by acrylates. As discussed in Chapter 1, off-line synthesis allows the manufacture of polyacrylates with extreme characteristics of adhesion–cohesion balance. By mixing such polymers, blends with desired adhesive characteristics can be prepared (see also Section 8.2). The majority of solvent-based acrylics are polymer blends, but acrylic HMPSAs based on polymer blends were proposed also. Mixing of water-based acrylics is a common method to achieve the desired adhesive properties. For instance, Acronal 4-D (BASF), the first soft acrylic dispersion patented in 1943, can be used as a tackifier for other acrylics.

Polymers that are chemically very different can be mixed also. For instance, PVEs can be used as tackifiers for NR, SBR, and acrylics.

Tackification with viscous polymers uses polymers with a pronounced viscous character, which act like plasticizers or liquid resins or soften the base polymer [14]. Macromolecular derivatives of butene/isobutene are the most important representatives of the viscous polymeric tackifiers.

Compounds used as tackifier resins are low-molecular-weight (400–2,000) polymers or monomers that are glassy, amorphous materials in the solid state. In special cases, such compounds can be low-molecular-weight derivatives of common plastomers (e.g., vinyl-aromatic polymers). Formulation with special plastomers (e.g., ethylene derivatives or NVP derivatives) is carried out to improve other characteristics like migration, water-solubility, and viscosity [14].

Generally, tackification is carried out using resins or plasticizers.

8.2.1.1 Tackification with Resins

The formulator must clarify the scope of tackification with resins, the parameters influencing tackification, and the effect of tackification on other (nonadhesive) performance characteristics of the PSA. In Ref. [14], the scope of tackification with resins, the theoretical basis of the tackification with resins (global and partial tackification), the criteria for the choice of tackifier resin (e.g., compatibility, polarity, aliphatic/aromatic ratio, molecular weight and MWD, softening point, and chemical composition) were discussed in detail. The main grades of tackifier resins and their characteristics (e.g., molecular weight, M_w/M_n, chemical composition, polarity, and color) are discussed in detail in Ref. [15], where resin dispersions, their formulation, manufacture, and stability are also described. The main tackifier resin classes (e.g., rosin derivatives, hydrocarbon resins, coumarone–indene resins, polyterpenes, terpene-phenolic resins, ketone resins, reactive resins, and hybrid resins) are discussed in detail. An economic comparison of tackifier resins is also given.

The influence of the base elastomer on tackification and suggested tackifier resins for various base elastomers (e.g., CSBR, chloroprene, acrylics, EVAc, and SBCs) were described in Ref. [15], where the most important resins used for tackification of SIS, SBS, and SEBs were also presented. Table 8.7 lists the main tackifier resins used for PSAs. In Ref. [15], the optimum tackifier concentration for various polymers (e.g., NR, acrylates, VAc copolymers, propylene copolymers, thermoplastic elastomers, and silicones) was also suggested. Reinforcing with resins, tackification for processing, tackification for postcuring, and the limits of tackification with resins were discussed. The main tackifier classes (e.g., rosin, hydrocarbon, and polyterpene resins) were described in Ref. [45]. A comparative evaluation of acid rosin and rosin esters and hydrocarbon resins is given. Tackifiers and tackification of SBCs and acrylic block copolymers is described by Yu and Paul in Chapter 3. Tackifier resins are discussed by Martín-Martínez in Chapter 2.

Tackification must promote bond formation and make bond rupture difficult. The main requirements for a tackifier are low molecular weight, high T_g, and compatibility. Generally, tackification lowers the modulus (due to increased entanglement molecular weight, M_e) and increases the T_g. Lowering of the modulus decreases the shear resistance [45]. As discussed in Ref. [14], tackification of NR differs from tackification of TPEs. Tackification of NR allows simultaneous increase of tack and peel and covers the whole polymer; tackification of TPEs does not lead to simultaneous increase of tack and peel, does not cover the whole polymer, and may produce increased the shear resistance. A compatible tackifier works like a solvent, whereas an incompatible tackifier works like a filler. For such a "solution," a two-phase structure was admitted. Although such a structure was experimentally confirmed, it was not characterized sufficiently. Considering the tackified elastomer a polymer solution in the resin and the polymer solution ideal (zero excluded volume effect), the plateau modulus (G') decreases as a function of the volume fraction of the polymer (V_p), the density of the blend (ρ), and the molecular weight between the entanglements (M_e) according to the following equation [62]:

$$G'_n = (\rho RT/M_e)V_p^2 \tag{8.5}$$

Tackification decreases the storage modulus (G') and increases the loss modulus (G''). It is admitted that for a given softening point and concentration of the resin, the higher

TABLE 8.7 Tackifyer Resins Used for Formulation Purposes

Resin Type		Trade Name	Softening Point (°C) Drop	R&B
Rosin	Gum	—	—	78
	Hydrogenated	Staybelite	75	68
	Glycerine-hydrogenated	Staybelite Ester 10	—	—
		Dermulsene DEG	83	—
	Glycerine-highly stabilized	Foral 85	82	—
	Hydroabietyl phtalate	Cellolyn 21	—	—
	Pentaerythritol wood	Pentalyn A	111	—
	Pentaerythritol hydrogenated	Pentalyn H	104	—
	Pentaerythritol-highly stabilized	Foral 105	104	—
	Polymerized	Poly-pale	102	95
	Tal oil	—	—	80
	Wood	—	81	73
Hydrocarbon	Olefin	Hydrolin	—	100–135
	Cycloaliphatic hydrogenated olefin	Permalyn	—	85–135
	Aliphatic petroleum HC	Piccopale/Piccotac	—	70–122
	Modified aromatic HC	Hercotac AD	—	85–115
	Styrene	Piccolastic	—	50–190
	α-Methyl styrene	Kristalex	—	25–120
	α-Methyl styrene–vinyl toluene	Piccotex	—	75–120
	Dicyclopentadiene	Piccodiene	—	73–140
	Mixed olefine	Statac, Super Statac	—	75–105
		Wingtack	—	—
	α-Pinene	Piccolite	—	10–135
	β-Pinene	Croturez, Piccolites	—	10–135
Terpene	—	Zonarez, Nirez 100	—	10–145
Terpene–phenolic	—	Piccofyn	—	100–135
	—	Dermulsene DT 75	—	—
Coumarone–indene	—	Cumar	—	100

the increase of the tan δ (G''/G'), the better the compatibility. At high frequencies during debonding, the resin stiffens the system. The T_g increases, as does the elastic modulus. The lower the modulus at low frequency and the higher at high frequency, the better the adhesive.

8.2.1.1.1 The Influence of the Base Elastomer on Tackification

Tackification with resins depends on the elastomer or viscoelastomer to be tackified. Principally, the ease of tackifying depends on the value of the modulus of the base elastomer. Theoretically, SBCs have a lower modulus value (10^6) in comparison to unvulcanized rubber (10^7); therefore, principally, their tackification seems easier. TPEs are segregated compounds in which tackification may involve the end-blocks, the mid-blocks, or both (see Chapter 3). For instance, HMPSAs generally contain two different

grades of resin, end-block compatible and mid-block compatible. Because of the segmented construction of such elastomers, their tackification (as increased tack) concerns the diene sequence only; that is, generally only "half" of the molecule can be tackified. Most tackifying resins are molecules that have a low molecular weight and a T_g above ambient temperature, typically near 40 to 50°C. In SBCs, these tackifiers increase the T_g of the mid-block (yet keep the value below ambient temperature) and enable the adhesive to behave viscoelastically at room temperature. They also reduce the rubbery modulus of the tackifier–SBC blend by plasticizing the rubbery matrix and increasing the fraction of the rubbery phase [63–65].

Hooker and Creton [66] studied SIS-based PSAs and elucidated the mechanism of how tackifiers improve adhesion. They determined that the highest adhesion values were observed when cohesive failure occurred, as opposed to interfacial failure or cavitation initiating at the interface. This agrees with the general observation that misleadingly high peel values are usually observed for adhesives that exhibit cohesive failure rather than interfacial failure. They noted that it is beneficial for the PSA to maximize strain without reducing the maximum stress. From a viscoelastic standpoint, this means softening the adhesive at high extensions and low deformation rates (during debonding), while maintaining or increasing the stiffness of the adhesive at small extensions and high deformation rates (during debond initiation). Tackifiers accomplish this by increasing the T_g and raising the modulus at high strain rates, while diluting the entanglements of the rubbery phase. For SBCs, this argument assumes that the tackifier resin is compatible with the midblock.

The base elastomer affects tackification by its chemical nature (polarity), molecular weight and MWD, modulus, T_g, and structure. Tackifying versatility for various base elastomers was discussed in Refs [14,45]. For solvent-based systems, the tackifying versatility decreases as follows [45].

$$\text{NR} \gg \text{CNR} > \text{APP} > \text{BR} > \text{SIS} > \text{SBS} > \text{SBR} \tag{8.6}$$

For water-based systems, the tackifying versatility decreases as follows.

$$\text{AC} > \text{CSBR} > \text{NR} > \text{CNR} > \text{BR} > \text{EVAc} > \tag{8.7}$$

8.2.1.1.2 The Choice of Tackifier and Its Influence on Tackification

Chu and coworkers [67–71] conducted some of the first research examining how tackifiers affected the viscoelastic properties of adhesives. They studied the influence of tackifier chemistry [67], molecular weight [68], and concentration [69] on the viscoelastic and rheologic properties of NR-based, styrene–butadiene rubber-based, and SIS-based adhesives. They also looked at how viscoelastic behavior was affected by a mid-block-associating tackifier [70], as well as an end-block-associating tackifier [71]. Class and Chu [67] determined that the tackifier and base polymer must have similar chemistry to be compatible. However, tackifiers that were expected to be compatible based on the chemistry demonstrated evidence of incompatibility above a critical molecular weight [68]. Class and Chu also reported that the tackifier became immiscible with the rubbery phase at a critical concentration. Immiscibility was evident from the two glass transitions (of the rubbery matrix) observed from rheologic measurements and the

microstructure determined from microscopy. However, Class and Chu did not examine how the resin characteristics affected the adhesive performance. Readers interested in a review of the chemistry of tackifying resins are referred to the works of Donker [72] and Benedek [14,45].

As discussed in Ref. [14], criteria for the choice of tackifier resin include compatibility, polarity, molecular weight and MWD, chemical composition, and softening point of the resin. Table 8.8 lists the main parameters of tackifier resins and their effect on the chemistry, adhesive, and converting properties of PSAs.

Generally, compatibility is influenced by the chemical nature, macromolecular characteristics (molecular weight and MWD), and concentration of the components [14,45,73]. Rubber–resin compatibility for HMPSAs tackified with mid-block, end-block, and "both block" compatible resins was discussed by Park [25]. Usually, suppliers give the compatibility characteristics of the tackifier resins with different polymers and with other resins at different ratios (e.g., 25/75, 50/50, and 75/25). Compatibility of the base elastomer and tackifier depends on the tackifying technology. Kajiyama [74] noted that the phase structure of PSA, mixed in the monomer state with the tackifier and solution polymerized, was different than that expected from the phase diagrams of solution-blended systems. O'Brien et al. [75] demonstrated that resin chemistry (aromaticity) affects adhesive morphology and performance of SBC-based adhesives and that atomic force microscopy (AFM) is an invaluable tool to gain fundamental understanding of the structure–property relationships of these soft materials. AFM images confirmed the

TABLE 8.8 Parameters of Tackifier Resin and Their Effect

Resin Characteristics	Depends on	Affects
Glass transition temperature	Polymer synthesis	Softening point Adhesive properties
Compatibility	MW, MWD Tackification technology	Adhesive properties
Polarity	Polymer synthesis	Compatibility
Molecular weight	Polymer synthesis	Compatibility
MWD	Polymer synthesis	Compatibility
Chemical composition	Polymer synthesis	Compatibility
Softening point	Polymer synthesis	Adhesive properties Viscosity Temperature resistance Optimum resin concentration Mixing technology Converting properties
Aromaticity	Polymer synthesis	Compatibility with styrene domains Site of block-association SAFT Holding power UV-transparency
Concentration	Required adhesion properties Economic considerations Radiation absorbance	Adhesive properties Processing technology Price

existence of styrene domains imbedded in a matrix, suggesting that the rubbery matrix is not composed of a single phase. Rheologic evidence also supports the existence of a two-phase rubber matrix from the bimodal tan δ curve. The rubbery matrix is likely composed of a tackifier-rich phase and an isoprene-rich phase. The effect of varying the tackifier aromaticity on the adhesive performance, rheology, and morphology of styrenic block copolymer-based PSA tape formulations was investigated, and it has been noted that increasing the aromaticity of the tackifier improved the compatibility between the tackifier and styrene domains. As a consequence, the high-temperature cohesive performance measured by the shear adhesive failure temperature (SAFT) decreased. A decrease in SAFT was due to plasticization of the end-blocks by the aromatic resins. The decrease in SAFT correlates well to the tan δ = 1max measured by rheology. The glass transition of the rubbery matrix was unaffected by the resin aromaticity. Significant differences in tack, peel resistance, and holding power due to resin aromaticity were not detected. Interestingly, the holding power of the adhesive formulated with the most aromatic resin is significantly greater than the other less aromatic resins. It is supposed that increasing the aromaticity of the resin somewhere between 7.5 and 14.8% [measured by nuclear magnetic resonance (NMR)] causes the resin to change from a mid-block-associating resin to an end-block-associating resin. End-block-associating resins increase the room temperature shear strength by increasing the size of the styrene domains and by increasing the relative volume fraction of the glassy phase. These glassy spherical domains, of course, act as physical cross-links and increase the holding power. Another means to increase holding power is to use a resin that is immiscible with the rubbery matrix. In this case, the resin forms incompatible glassy domains in the rubbery matrix that behave similar to a reinforcing agent or filler. In fact, some incompatibility of the resin can lead to higher shear strength and holding power. However, the tackifier and elastomer must be compatible enough that the tackifier does not begin to separate into yet another phase that would severely degrade adhesive performance and stability. A formulated four-arm "all acrylic" block copolymer with radial architectures, based on poly(2-EHA-co-methyl acrylate) and polymethyl methacrylate (PMMA) demonstrates a strong increase in shear resistance with the amount of tackifier [76].

A new concept for the characterization and selection of resins based on the polarity of the resin was developed [14] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). To determine which base polymers are compatible with which tackifier, it is useful to characterize tackifiers and the base polymers by their relative aromaticity and polarity. Aromaticity can be analyzed via NMR spectroscopy to determine the relative number of protons attached to an aromatic ring or via cloud point determinations using an appropriately chosen solvent system. Relative polarity and aromaticity can be determined using the diacetone alcohol–xylene (DACP) cloud point or methylcyclohexane–aniline (MMAP) cloud point, respectively [77].

The addition of tackifier resins improves the tack and peel resistance of elastomers. Such an increase depends on the tackifier level and the softening point of the resin. The relationship between resin softening point and resin concentration at which maximum performance is obtained was discussed in Ref. [14]. Recent synthesis of special block copolymers leads to soft elastomers that require a lower level of tackifier. For instance, Smit et al. [78] investigated anionically synthesized block copolymers with methyl

methacrylate (MMA) hard blocks and a BA soft mid-block. In their tackified formulations, the polymer level ranges from 10 to 45%. In contrast, formulation of common WB acrylics use 10–30% tackifier at most. Simal et al. [76] used a four-arm "all acrylic" block copolymer based on poly(2-EHA-*co*-methyl acrylate) and PMMA up to 75% tackifier.

The influence of low-softening-point resins and of high-cohesion acrylics and liquid tackifier resins on adhesive characteristics was discussed in Ref. [45]. However, the influence of the softening point of the resin must be examined with criticism. As noted by O'Brien et al. [75], experience and tradition within the PSA industry indicates that the T_g [whether measured by ring and ball softening point (RBSP), drop point, dynamic mechanical analysis (DMA), or differential scanning calorimetry (DSC)] of the tackifier has a significant influence on adhesive properties. Indeed, empirical evidence such as Dahlquist's and Fox's equation indicate that the T_g of the system is critical in adhesive performance and is influenced by the T_g's of the individual components. In practice, however, these thermal transitions are only weakly expressed and the precision of any determination is probably not better than ± 2°C. Therefore, to confidently make a correlation between T_g, RBSP, or rheology and adhesive performance, the difference in T_g between samples should probably be on the order of 5°C. In practice, this is impractical because the T_g of an aliphatic hydrocarbon resin is not an independent variable and is not directly subject to experimental control.

The choice of the tackifier resins strongly depends on the available mixing technology also (see also Chapter 10). Suggested tackifier concentration for the main elastomers and viscoelastomers, as a function of the product class, product application, and adhesive status, as well as screening formulations for tackification, are listed in Ref. [14]. The use of soft resins for tackification of water-soluble PSAs is discussed by Czech in Ref. [31]. Suggested application domains for water-based tackifier dispersions are listed in Ref. [16]. A comparison of tackification with solvent-based, water-based, liquid, and molten resins is given by Benedek in Ref. [45].

Tackification influences other formulation modalities as well. Such influence is reflected in tackification for postcuring by the formulation of radiation-curable compositions. Generally, because the resin is a diluting agent in the polymer matrix and reduces the number or cross-link-points, there is an upper limit of the amount of resin that can be added, delimited by shear reduction. By radiation-curable compositions this limit is affected through the radiation absorbance of the resin [14]. Therefore, for tackified formulations the radiation dosage must be increased and technologically adequate resins must be chosen. For instance, saturated hydrocarbon resins are more effective than their unsaturated counterparts in their ability to enhance EB cross-linking of styrene–isoprene (SI) block copolymers.

As noted in Ref. [14], in optimization of the tackifier level discrepancies may appear because of the different sensitivity of the adhesive characteristics toward tackification. The best values of a given adhesive characteristic (e.g., peel resistance or tack) may differ according to the test method (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Optimum tack, peel resistance, and shear resistance are obtained at different resin levels.

For the same formulation, peel resistance, loop tack, polytack, and shear resistance achieve the optimum values for a different range of disproportionated rosin acid,

hydrocarbon resin, and hydrogenated rosin ester. The limits of tackification with resins are discussed in Ref. [14]. Tackifier resins were discussed in Refs [14,25,45,46]. Tackifiers for SBC-based PSAs (e.g., rosin resins, terpene resins, and hydrocarbon resins such as aliphatic, C5 hydrocarbon resins, aromatic, C9 hydrocarbon resins, dicyclopentadiene hydrocarbon resins, hydrogenated hydrocarbon resins and hydrogenated, C9 hydrocarbon resins) were described in Ref. [25].

The particular features of tackification with resin dispersions were discussed by Benedek in Ref. [45]. A wide range of technically equivalent (i.e., yielding the same adhesive properties) tackifier dispersions is available. Differences exist concerning the dispersion properties (processibility) and logistical and economical benefits. For water-based systems there are some parameters that override the effect of softening point and molecular weight of the base polymer.

Advances in tackification of SBCs and novel acrylic block copolymers are described by Hu and Paul in Chapter 3.

8.2.1.2 Tackification with Plasticizers

Plasticizers such as oils are also used to fine-tune the adhesive properties by reducing the T_g, stiffness, or viscosity [79]. Tackification with plasticizers can be carried out as a main process, but it can also occur simultaneously with tackification with resins [14,45]. Typical resin dispersions contain 40–60% resin and 2–20% plasticizer. It is evident that when such tackifiers are used, plasticizers are also added in the formulation. Some tackified–plasticized formulations can contain a high level of plasticizer, comparable to tackifier level. For instance, adhesive formulations based on chlorinated rubber (90 pts) include a plasticizer (29 pts) and a tackifier resin (35 pts). Such compositions can contain chlorinated rubber (60 pts), together with polyvinyl butyral (10 pts), phenolic resin (45 pts), and plasticizer (90 pts).

In a different manner of tackification with resins, the aim of tackification with plasticizers may be other than increased tack (see also Table 8.3). For instance, formulating for removability achieves softening of the polymer with the plasticizer or other viscous components. For PSAs formulation with plasticizers is generally carried out for softening of the bulk (coated) adhesive or reduction of the viscosity of the coatable adhesive. The majority of cross-linked formulations contain a plasticizer, intended to make it easier for the polymer chains to slide over each other. The influence of plasticizers on removability was discussed by Czech in Ref. [28], where the use of various plasticizers at different levels for removable formulations was investigated.

The tackifying mechanism and the influence of the tackifying agent on T_g is quite different for plasticizers and tackifiers. Plasticizing reduces the modulus and the T_g. Tackifier resins may increase tack without an important decrease in shear resistance; plasticizers increase tack, but lower cohesion. Various micro- and macromolecular compounds were used as plasticizers. The fraction of the polymer that has a molecular weight less than twice the entanglement molecular weight (M_e) will act as a plasticizer. The mechanism of plasticizing and the role of compatibility in plasticizing was discussed by Benedek in Ref. [14].

The special mechanism of plasticizing acrylic hydrogels (the plasticizer causes the transition of debonding type from solid-like to fibrillar and increased adhesion as a

function of its hydrophilicity) was described by Feldstein et al. in Ref. [80]. The role of water as a plasticizer was discussed as well. Plasticizers for methacrylic polyelectrolytes are described by Feldstein et al. in Chapter 7.

Common plasticizers and oils as plasticizers were described by Benedek in Ref. [14]; the role of oils and the choice of oils were discussed. The use of liquid resins and liquid polymers (e.g., polybutenes and PIBs) as plasticizers was discussed as well (see also Chapter 4). Plasticizers can influence cross-linking of the formulation [14]. The use of plasticizers in water-soluble PSAs was discussed by Czech in Ref. [31]. Water-soluble plasticizers were also described by Benedek in Ref. [15]. Plasticizers in vinyl film can have a pronounced effect on adhesive properties during the aging process; therefore, plasticizer-resistant adhesives must be selected. Plasticizer resistance was the subject of Refs [14,60] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Antimigration agents were presented in Ref. [15]. Plasticizers are also described in Chapter 2 by Martín-Martínez and in Chapter 5 by Foreman.

8.2.1.3 Tackification with Other Compounds

Tackification with elastomers, viscoelastic polymers, viscous polymers, and plastomers was discussed in detail in Ref. [14]. The addition of diblocks and, more recently, polyisoprene to SBCs led to enhanced tack and wetting properties [81,82] (see also Table 8.4 and *Fundamentals of Pressure Sensitivity*, Chapter 5).

8.2.1.4 Detackification

Principally, detackification is the result of the excessive immobilization of macromolecules [45]. Tackification is required mainly for permanent adhesives; detackification is needed for removable compositions (see also Section 8.1.1.3). Tackification is a general formulating method, and detackification is applied in special cases only. Detackification uses special additives, resins, cross-linking agents, fillers, and abhesives. Detackifying resins are known as well. Detackifying agents must work on the bonding surface. Detackification was discussed by Benedek in Refs [14,15]. The use of stearinic acid as a detackifier for removable formulations was discussed by Czech in Ref. [28]. Screening formulations with various detackifiers (e.g., silicone derivative, wax, and VAc copolymer) were presented in Ref. [14]. Detackifying polymeric fillers were discussed in Ref. [46].

8.2.2 Cross-Linking

A formulation for better cohesion can be achieved by increasing the molecular weight, cross-linking, and reinforcing. Principally, reinforcing is achieved by fillers, cross-linking, or using associative tackifiers. Why to cross-link and how to cross-link? The general aim of cross-linking as a modality to create intramolecular segregation is illustrated by NR. Such intramolecular or intermolecular segregation offers the potential to regulate the plasticity/elasticity balance and, thus, to improve the time/temperature-dependent mechanical performance characteristics of the polymers. As mentioned previously, such segregation is achieved with a cross-linked network, crystalline structure, or reinforcement with fillers. The construction of segregated structures determines their mobility and elasticity (see Table 8.9).

TABLE 8.9 Parameters of Formulation for Cohesion Increase

Parameter	Effect by	Segregation Method	Compound	Influence on
Molecular weight	Modulus	—	NR, AC, PB, silicones	Tack, peel, shear, cuttability, dimensional stability
Segregation due to chemical composition	Reinforcing	Cross-linking		
		Built-in cross-linked structure	NR, CSBR, TPE, AC	Adhesive properties, cuttability, shrinkage, temperature resistance
		Built-in cross-linkable structure	NR, CSBR, AC, silicones	Adhesive properties, coating technology, cuttability, shrinkage temperature resistance
		Filling		
		Nonreactive fillers	NR, AC, Hydrogels	Adhesive properties, Viscosity, Cuttability
		Reactive fillers	NR	Adhesive properties
		Associative tackifiers	TPE	Adhesive properties
		Crystallization	CR	Adhesive properties

One of the current aims of cross-linking is to improve internal cohesion, given by the macromolecular and chemical characteristics of a polymer, which can be low *ab ovo* due to chemical synthesis or base formulation. For instance, the most used solvent-based acrylates for protective films have a glass transition temperature of about −20°C. The common base polymer for solvent-based acrylates is so soft that it is not possible to characterize it using Williams' plasticity test (see *Applications of Pressure-Sensitive Products*, Chapter 8). Such adhesives require cross-linking to improve internal cohesion. In past decades new products were developed that do not require external cross-linking. Such formulations generally contain at least two components; one of them, the base polymer, is harder (with a T_g of about +7°C). Such an adhesive is self-curable. The new self-cross-linking products exhibit Williams' plasticity of 2–2.8 mm (PN). A simple dispersion of silicone polymer and *MQ* resin can yield an adhesive with good peel and tack adhesion, but without cohesive strength and high-temperature properties. The formation of a network structure between the silicone polymer and *MQ* resin is required to achieve improved cohesive strength and lap shear properties. Some degree of molecular-weight building and polymer–resin bonding is done at the suppliers through a base-catalyzed condensation reaction using the silanol functionalities on the *MQ* resin and the terminal silanols of the silicone polymer. To fully develop the network structure and, therefore, the high-temperature property of the silicone PSA, further cross-linking is carried out at the end-user level [44].

As discussed in detail in Chapter 10, a slight mechanochemical destruction of the macromolecules of NR (by mastication), followed by post-cross-linking, leads to products with balanced adhesive properties (labels). A more advanced mastication and cross-linking, together with a higher coating weight, allow the better shear and high tack and

peel necessary for tapes. Thus, cross-linking may serve as a tool to regulate removability (see Section 8.1.1.2.3). A much higher degree of cross-linking and low coating weight lead to low-tack, removable products (i.e., protective films).

How to achieve cross-linking? The principles of cross-linking PSAs have been discussed by Benedek in previous books [14,15], which reported that cross-linking can be achieved chemically (see also Chapter 1) or physically (see also Chapters 1 and 3). Chemical cross-linking depends on the chemical composition and macromolecular build-up of the polymer and can be achieved using classic, chemically started reactions or by radiation. Cross-linking is also conditioned by application domain of the PSA (see *Applications of Pressure-Sensitive Products*, Chapter 4). Cross-linking is a formulation possibility based on built-in or formulated reactivity of the components of the PSA (see also Chapter 1). Formulation by cross-linking uses the reactivity of the macromolecular and micromolecular compounds in the adhesive recipe to build up or perfect a molecular or macroscopic network. The build-up of a network reduces the chain mobility and improves or reduces the elastic deformability of the macromolecular structure. As discussed previously, cross-linking occurs during polymer synthesis (for instance, during emulsion polymerization of dienes where gel is formed in the particles), and it is a tool to build up a polymer network, which ensures pressure-sensitive properties. Postsynthesis cross-linking of PSAs is used to control the adhesion–cohesion balance or to provide other converting or application properties. Cohesion increase plays a role mainly in shear-related applications and removability. The effect of cross-linking is always an increase in the cohesion of the adhesive. Such an increase may be moderate (to improve the peel resistance), pronounced (to increase the shear resistance), or excessive (to allow cuttability and die-cuttability) [14]. For instance, a non-cross-linked acrylic polymer has a storage modulus of about 10^3 Pa, and this value can be increased to 10^4 by irradiation. The use of cross-linking to regulate the adhesive characteristics for various PSPs with different adhesives and different cross-linking degree is discussed in Ref. [18]. Generally, anchorage on the carrier, removability, peel resistance, shear resistance, dimensional stability, temperature resistance, and converting properties are improved. The adhesive characteristics of acrylic tapes and labels cross-linked using different methods are listed in Ref. [18].

Some raw materials possess a built-in cross-linkable structure that works physically or chemically. The best known is NR, but synthetic elastomers (e.g., SBR or CSBR) possess cross-linked structures as well. Chemical cross-linking supposes the presence of reactive groups (polar functional groups or unsaturation) in the polymer. UV-light-induced cross-linking also requires a chemical composition of this type; EB-induced cross-linking does not. Cross-linking due to built-in macromolecular reactive sites is generally carried out using solvent-based PSAs. Here, the lengthy experience with cross-linking NR can be called upon (see Chapter 2). Cross-linking of solvent-based acrylates by conventional (chemical) curing and photoinitiated cross-linking are described in Ref. [45].

Cross-linking as a possibility to regulate polymer rheology is limited by the end use of a PSP. For instance, such a high degree of cross-linking as used for protective films is not practical for labels where high tack is required. Protective films possess a so-called application tack, that is, a tack value that, together with lamination pressure, helps to bond them to the substrate. The application of external cross-linking agents for common

water-based polymers that have built-in carboxy functionality (e.g., carboxylated acrylics or CSBR) causes a pronounced loss of tack and peel. This can be understood by considering the higher molecular weight of such compounds, their high content in hard comonomers, and their advanced cross-linking degree on the particle surface. The cross-linking possibilities of hot-melts are limited also; here, thermal cross-linking cannot be used.

As discussed in Chapter 1, although currently used in the off-line synthesis of special acrylics and their modification (by the use of cross-linkable formulations), the main application domain of curing is post-cross-linking, that is, the in-line synthesis (or modification) of the PSA (see also Chapter 1).

As with each formulation procedure, cross-linking is accompanied by side effects as well, which affect factors other than the adhesive properties. This is quite normal, because molecular cohesion is directly related to the mechanical properties of the polymer (see *Fundamentals of Pressure Sensitivity*, Chapters 2, 5, 7, and 11), and such performance characteristics are decisive for the conversion of PSPs (see Chapter 10).

Cross-linking affects coating technology due to its influence on the fluid adhesive. Generally, the adhesives for protective films are cross-linked formulations; special tapes also need a cross-linked PSA-formulation. Therefore, the coating machines for labels, tapes, and protective films exhibit different characteristics (see Chapter 10). The scope of cross-linking, the theory of cross-linking (role of cross-linking, parameters of cross-linking, and cross-linking of ordered structures), the cross-linking basis (functionality vs cross-linking agents, curing of SBCs, and radiation, curing), cross-linking of rubber–resin formulations, cross-linking of acrylics, cross-linking of segregated polymers, simultaneous cross-linking–plasticizing, and the limits of cross-linking were discussed in detail by Benedek in Ref. [15]. The influence of cross-linking on the adhesive properties was discussed in detail by Benedek in Ref. [17].

8.2.2.1 Chemical Cross-Linking

Chemical cross-linking includes both elastomer- and viscoelastomer-based PSA formulations. Chemical cross-linking is a characteristic for CSBR latices because they consist of a mixture of polymer species with linear chains, branched chains, and a cross-linked network. Their cross-linking during polymerization leads to gel structures, which negatively influence the adhesive performance characteristics. On the other hand, their functional (carboxylated) monomer content allows their postcuring. Many natural rubber–resin solvent-based formulations also contain a cross-linking agent. The effect of cross-linking may be illustrated by the increase in G'. Such NR-based formulations display acceptable adhesion–cohesion balance without cross-linking (due to the entanglements in rubber and its strain hardening). Generally, they can be replaced by cross-linked viscoelastomers only. First, cross-linked and uncross-linked rubber–resin adhesives were manufactured for protective films as solutions; later, solvent-based cross-linked and water-based cross-linked and uncross-linked acrylics were tested. However, to ensure low-application viscosity, such rubber–resin recipes used for removable (protection) films with a very low coating weight need premastication and post-cross-linking. Such rubber-based recipes include masticated NR and cyclized rubber, tackified with a low level of resins and cross-linked with isocyanates.

Isocyanates are also recommended as curing agents for solvent-based acrylic adhesives and polyaziridine or isocyanates (at a concentration of 0.3–2.0%) are used for water-based acrylics. The most commonly used external cross-linking agents are isocyanate derivatives, applied in a concentration comparable to the level of internal multifunctional cross-linking monomers (see also Section 8.2.4.1.2).The use of isocyanates, aziridines, and propylene imine as cross-linkers for removable formulation was investigated by Czech [28]. Chemical cross-linking of acrylics by cross-linking monomers and various cross-linking agents (metal acid esters, metal chelates, multifunctional isocyanates, polycarbodiimides, multifunctional propylene imines, and amino resins) were described in detail by Czech in Ref. [54]. Cross-linking agents are discussed by Martín-Martínez in Chapter 2.

Commercial as-supplied silicone PSAs exhibit good pressure-sensitive behavior immediately after solvent removal; however, further cross-linking is typically done to reinforce the adhesive network for improved high-temperature performance. Two cure systems are commercially available today for silicone PSAs: peroxide-initiated free-radical cure and platinum-catalyzed addition cure [44]. Key parameters in addition-curable silicone PSA compositions are variations in polymer structure, cross-linker structure, and resin molecular weight and structure. The PSA composition may further include organic diluents and additives that target specific requirements for lowering the thermal expansion coefficient, enhancing anchorage, or improving high-temperature properties. Temperature requirements for curing are also lower, allowing the use of temperature-sensitive substrates. However, addition-cured systems suffer from generally lower heat stability than peroxide systems. The literature describes improved compositions that utilize peroxide and addition dual-cure mechanisms or the use of antioxidants to improve high-temperature performance [83,84].

As discussed in Ref. [15], reactive resins can be used for cross-linking also. Such compounds are functionalized common resins or special synthetic products with reactive groups.

A special case of simultaneous cross-linking and tackification was demonstrated by Feldstein et al. [80] for pressure-sensitive hydrogels. In this case, interpolymer complexes (ladder-like and carcass-like) are formed due to hydrogen, ionic, or electrostatic bonding. Thus, from hydrophilic, water-soluble polymers a water-insoluble hydrogel (ladder-like complex) or water soluble polymer (carcass-like complex) is built up (see also Chapter 7).

8.2.2.2 Radiation-Induced Cross-Linking

In a similar manner to chemically induced cross-linking, UV-light induced cross-linking needs reactive chemical sites in the polymer; EB-curing does not require them (see Chapter 1). Generally, UV-induced cross-linking needs a photoinitiator as well (see Table 1.1 in Chapter 1).

In the classic technology, using an external photoinitiator, the liquid monomers are applied to the carrier with a doctor blade or by roller coating or spraying and cured in a polymerization tunnel from which oxygen has been excluded. Developments in macromers allow the use of oligomers and macromers instead of monomers, with a processible viscosity at 90–120°C. Raw materials (monomers and oligomers) for 100% solids

were described in Ref. [14]. In this reference book UV-light-curable multifunctional monomers were suggested for acrylics (e.g., dicyclopentadienyl acrylate, polybutanediol diacrylate, β-carboxyethyl acrylate, 3-chlor-2-hydroxypropyl acrylate, thiodiethylene glycol diacrylate, and isobornyl acrylate); EB-curable monomers were noted for acrylates (e.g., HDDA, TMPTA, TGPTA, PETA, and triallycianurate) and for SBCs (e.g., pentaerythritol triacrylate and trimethylol propane thioglycolate for SIS and SBS). The oligomers (50–10%) in the recipe can possess various chemical compositions (hydrocarbon based or heteroatom based) and different functionalities. Thus, they can undergo various types of reactions (e.g., polymerization, polyaddition, and polycondensation) that lead, through different initiation mechanisms (thermal or radiation induced), to various polymers.

The most used radiation-curable oligomers are polyester acrylates, epoxy acrylates, urethane acrylates, and polyether acrylates. Compounds with acrylate and vinyl functionality (e.g., polybutadiene diacrylate, methacrylate terminated Pst, and hydroxyl-terminated polystyrene) can be used for EB curing. The molecular weight of the formed polymers should differ according to MWD. For a narrow MWD a weight average molecular weight of 100,000 and for a broad MWD a molecular weight of 140,000 are required to enable the desired response to EB curing. In general, constituents with a molecular weight of less than 30,000 are nonresponsive to EB radiation [85].

A special domain of UV-light-induced curing is based on reactive acrylic oligomers with a built-in photoinitiator (supplied as "warm" melts, e.g., Acronal-DS-3429; see also Chapter 1) and the so-called Kraton liquid polymers, with hydroxyl and oxirane functionalities (see also Chapter 3). Acrylic oligomers and macromers are described in Ref. [14,15,28]. UV-cross-linkable PSAs have a pendant photoinitiator group in the polymer backbone of PSA; cross-linking occurs with neighboring groups when UV light irradiated.

The main problems with UV-light-induced photopolymerization are the need for polymerizable functionalities, a photoinitiator, and an adequate level of radiation (see also Table 1.5 in Chapter 1). The nature of the initiator strongly influences the energy transfer during initiation, the side reactions due to atmospheric oxygen, and the residual unsaturation. The most important photopolymerization mechanisms are free radicalic or cationic. Cationically photopolymerizable monomers are listed by Do and Kim [55]. The thiol-ene system is a photoinduced addition of a thiol (RSH) to olefinic double bonds through a chain transfer process in the presence of a photoinitiator. Polymerization of thiol-ene initiated systems is not inhibited by oxygen and the polymerization system works without diluent. This method can be used for SBCs with a triblock sequence with pendant vinyl groups.

The main possibilities of building in UV-light-sensitive photoinitiators in polymers are copolymerization with an unsaturated photoinitiator (monomer), the use of a multifunctional photoinitiator with two photoreactive sites, and side-chain modification of polymerized PSAs with derivatives containing double bonds. In practice, multifunctional photoinitiator homo- or copolymers are prepared and mixed with common polyacrylates.

The polymerization techniques for UV-polymerizable PSAs from thickened monomer blends and prepolymerized monomer mixtures were described by Benedek in Ref. [46], and the manufacture of UV-cross-linkable PSAs is discussed as well. The kinetics of

UV curing was investigated by Do and Kim [55]. Thermal curing can be combined with radiation-induced curing.

A complex cross-linking system for an optically clear PSA used as a mounting aid in electronics, which includes various mechanisms, is described by Chang and Holguin in *Applications of Pressure-Sensitive Products*, Chapter 3. Using different chemistries and curing processes, an optically clear adhesive was developed for the needed complex transition from a removable PSA to a permanent PSA and finally to a structural adhesive for this application. The first stage of product manufacturing utilized ionic cross-linking of the acrylic polymer during the coating and drying phases. The second stage used UV curing for cross-linking the urethane oligomer, which forms an interpenetrating network, and the third stage used thermal curing to completely cross-link the acrylic polymer. Such progressive transformation to different types of adhesives is monitored and confirmed by the shift in viscoelastic window. The main component for the curable PSA layer is a solvent-based PSA with acid and epoxy functionality. This adhesive was combined with an acrylated urethane oligomer, a methacrylated silane thermoset cross-linker, a photoinitiator, and a metal chelate ionic cross-linker, forming the adhesive blend for the curable PSA layer.

8.2.3 Filling

There are a number of benefits to be gained from adding a filler, such as reducing adhesive costs, improving rheology, and improving conversion properties. Molecular flexibility can be controlled by T_g, cross-link density, plasticizers, flexibilizers, and fillers. A simplified approach explains the functioning of networks in TPEs compared with filled liquids (see also Chapter 1). This approach assumes that the filler particles are more mechanically resistant than the liquid and that they do not interact with the matrix. This is not always true. In some cases, fillers are used like polymer blocks in a segregated structure to improve cohesion. Such an effect can be improved through the use of reactive fillers [15]. Fillers can modify the rheology of viscous or viscoelastic systems without affecting their viscous character or they can build up an elastic network in such systems, transforming them into viscoelastomers or elastomers. On the other hand, excessive filling leads to a plastomer–duromer character [15]. The result of filling depends on the nature of fillers and on the filled system. Filled systems are special composites in which various components can act as fillers. In several cases, such systems behave like a network. Partially crystalline structures can be considered amorphous systems filled with crystallites; thermoplastic elastomers were described as elastomers containing polystyrene blocks as filler, and certain reactive fillers build up interchain bonds, providing a real network. Such networks improve the cohesion of the polymer. There are nonreactive fillers working physically and reactive ones that can build up a chemically linked network (see also Section 8.2.3.2.3).

The formulation of pressure-sensitive hydrocolloids using liquid crystalline polymers and nanoparticles of montmorillonites that form hydrophilic channels to intense moisture transportation from skin surface into the depth of a dressing or patch was discussed in detail by Kulichikhin et al. in Ref. [35]. The most important fillers suggested for PSAs and their working mechanism are described by Martín-Martínez in Chapter 2.

8.2.4 Formulation with Additives

As discussed in Section 8.1.5, formulation is technology-related; that is, it must allow the processing of the adhesive and of the PSP (see also Table 8.1). Therefore, special (nonadhesive) additives are included in the formulation. Some impart chemical properties (reactivity or inertia) to the formulation, whereas others ensure the technological performance characteristics of the adhesive (coatability, convertibility, etc.). Table 8.10 lists the main additives used in formulation of PSAs and PSPs.

8.2.4.1 Formulation with Chemical Additives

Chemical additives react with the main polymers of the formulation. They are reactive compounds used to ensure storage, light, and temperature stability (e.g., antioxidants and light protection agents); to initiate cross-linking (e.g., cross-linking agents); to initiate polymerization, etc. Chemical additives used for PSAs were described in detail by Benedek in Ref. [15]. Such compounds include cross-linking agents, photoinitiators, antioxidants and light protection agents, fillers, plasticizers, compatibilizers, detackifiers, and flameproof agents.

8.2.4.1.1 Protective Agents

Protective agents used to ensure environment- and time-dependent storage stability of PSAs were described by Benedek in Refs [15,45]. Aging stability of PSAs on different chemical bases was discussed in Ref. [17]. The test of aging is described in *Applications of Pressure-Sensitive Products*, Chapter 8. Such additives include antioxidants and light protection agents (see also Chapters 2 and 3). Antioxidants improve the weathering and thermal and light resistance of components of PSPs. Autooxidative degradation can be reduced by heat stabilizers: primary and secondary antioxidants. Primary antioxidants (e.g., hindered phenolics and secondary amines) act as proton donors. Secondary antioxidants (e.g., thioesters or phosphites) reduce the hydroperoxides formed during oxidation. The main antioxidants (commercial name and chemical composition), their suppliers, the suggested application domains, and levels are listed by Benedek in Refs [15,45]. Color stabilization is also discussed. In Ref. [46], the whole range of antioxidants used for PSPs (i.e., for the adhesive and the carrier material) was discussed. Antioxidants used for rubber–resin PSAs are discussed in detail by Martín-Martínez in Chapter 2.

8.2.4.1.2 Cross-Linking Agents

Generally, cross-linking agents react with the base polymer. Such agents include catalysts, initiators, multifunctional monomers, etc. Built-in or external cross-linking agents can be used. Cross-linking agents used for thermally or radiation-induced curing of PSAs were discussed in detail by Benedek in Refs [15,46]. Their application domain and protection function were described also. Polyaziridines, epoxies, aminoplasts (e.g., melamine–formaldehyde resins), metal salts or oxides, and metallic chelates can be used as external cross-linking agents. The most often applied cross-linking agents for solvent-based PSAs include isocyanates, epoxides, amine derivatives, and carbamide resins. Cross-linking agents (e.g., metal chelates, metal acidesters, multifunctional isocyanates, polycarbodiimides, and amino resins) used for solvent-based acrylates as

TABLE 8.10 Additives Used in Formulation of PSAs and PSPs

Additives	Effect	Chemistry	PSA	Carrier
Chemical				
Cross-linking agents	Thermal- and radiation-induced cross-linking	Organic, inorganic compounds multifunctional monomers	•	—
Photoinitiators	UV-light induced cross-linking	Hydrogen abstractors, α-cleavage, multifunctional, polymerizable	•	—
Antioxidants	Storage stability, weatherability thermal stability	Primary (hindered phenolics and secondary amines) Secondary (thioeters, phosphites)	•	•
Light protection agents	Storage stability, weatherability		•	•
Tackifiers	Adhesive properties	Natural and synthetic resins	•	•
Detackifiers	Adhesive properties	Fatty acid derivatives, release agents, PVA	•	—
Plasticizers	Adhesive properties	Special, liquid esters,water	•	•
Solubilizers	Water solubility	Water-soluble polymers, oligomers, plasticizers	•	—
Compatibilizers	Blending ability	Special polymers	•	•
Flameproof agents	Flame resistance	Halogenated derivatives, metallic oxides	•	•
Fillers	Cohesion control	Inorganic salts, oxides, silicates,	•	•
Technological				
Solvents	Dispersant, viscosity control, thickener, adhesion promoter	Low molecular organic compounds, monomers, water	•	—
Oils	Viscosity control, defoamer	High flame point solvents	•	—
Tackifiers	Viscosity control	Resins	•	—
Plasticizers	Viscosity control	Special, liquid esters	•	—
Fillers	Viscosity control, costs reduction	Inorganic salts, oxides, silicates, metals, carbon black, water, air	•	•
Antistatic agents	Converting properties	Organic salts	•	•
Antiblocking agents	Converting properties	Inorganic fillers		•
Release agents	Converting properties	Silicones, carbamate derivatives PVA, PVAc	•	•
Antimigration agents	Converting properties	PE homo- and cooligomers	•	—
Wetting agents	Coating properties, migration, adhesive properties	Ethoxylated amines, polyalkylene oxides, acetylenic diol, sulpho-succinate and succinamate derivatives	•	—
Protective colloids	Coating properties	Hydrophilic polymers	•	—
Defoamers	Coating properties	Silicone derivatives, acetylenic alcohol, oil	•	—
Thickeners	Coating properties, migration, antimicrobial stability	Solvents, fillers, acrylic polymers, ethoxylated derivatives, PVA, cellulose derivatives, polysacharrides, PUR	•	—
Viscosity-reducing agents	Coating properties	Carbamide derivatives	•	—
Humidifiers	Coating properties, converting properties	Polysacharrides	•	•
pH-Adjusting agents	Viscosity, mechanical stability drying, adhesive properties	Inorganic and organic bases, and acids	•	—
Antimicrobial agents	Storage stability	Organic salts	•	—

chemical cross-linking agents were discussed by Czech in Ref. [54]. Cross-linking agents are described by Martín-Martínez in Chapter 2.

8.2.4.1.3 Initiators

As mentioned earlier, UV-light-induced polymerization and curing require a photoinitiator, a mediator between the photopolymerizable compound and light. Generally, photoinitiators are special organic compounds able to abstract hydrogen and produce radicals, which initiate polymerization. Monomeric and macromolecular photoinitiators can be used as well. Photoinitiators are described in detail by Benedek in Ref. [15]. Photoinitiated cross-linking (by UV light) solvent-based acrylates were discussed by Czech in Ref. [54].

Photoinitiation with the aid of UV lamps and UV lasers and photoinitiators (α-cleavage, hydrogen atom abstracting, multifunctional, and copolymerizable) was described. The influence of photoinitiators and selected cross-linking agents on solvent-based acrylics was investigated.

8.2.4.1.4 Other Chemical Additives

Compatibility can be improved using compatibilizers that interact with the noncompatible components of the polymer blends [15] (see also Chapter 5). Flameproof agents are nonignitive, or build up barrier layers. Various compounds can be used as flameproof agents (see Ref. [15]).

8.2.4.2 Technological Additives

Technological additives include compounds that ensure the solubilization (or dispersing) of the PSA to achieve a coatable fluid (e.g., solvents, oils, protective colloids, surfactants, antifoam agents, etc.) (see Chapter 1) and compounds that impart special properties to the finished PSP (e.g., solubilizers, flameproof agents, fillers). The main technological additives (e.g., wetting agents, such as surfactants and cosolvents, neutralization agents, viscosity regulators, such as thickeners and viscosity reducers, stabilizers, solubilizers, humidifiers, antimigration agents, cuttability agents, and solvents) were described by Benedek in Ref. [15]. Antiblocking agents and slip agents were described in Ref. [46]. They affect the corona treatment of films (see also Chapter 10) and printing.

8.2.4.2.1 Solvents and Dispersing Media

Solvents are used as temporary components of the adhesive, primers, release coatings, printing inks, and curing agents [15]. Raw material-dependent formulation uses various dispersing/solving media to ensure the fluid state of the adhesive. Some of the adhesives are true solutions [e.g., rubber–resin PSAs (see also Chapters 1 and 3), certain acrylics (see also Chapter 5), PVEs, silicones (see also Chapter 6), and PURs] (see also Chapter 11); others are water-based dispersions [e.g., acrylics (see Chapter 5), VAc, carboxylated styrene-diene copolymers (see Chapter 1), and PURs] (see also Chapter 11) or solvent-based dispersions (e.g., PVEs).

The physical status of the adhesive depends on its off-line synthesis technology also. Some viscoelastomers are manufactured as solutions or dispersions (e.g., acrylics, VAcs); that is, their liquid status is given by the off-line synthesis. Others, like NR and the main part of synthetic elastomers, are supplied as a solid-state material and therefore must be

micronized and solved (see Chapter 10) before formulation. In this case, the solvent is the main technological additive used.

Solvents used as solving/dispersing media differ according to the type of raw materials. As an example, isoparaffinic solvents are used for NR, butyl rubber, poly-isobutene, ethylene-propylene rubber, and polyisoprene. The use of solvents imposes their recycling (see Chapter 10). Solvents are discussed by Martín-Martínez in Chapter 2.

As mentioned earlier (see Section 8.1), HMPSA formulations incorporate a high level of plasticizer, usually a naphthenic oil or a liquid resin. The oil used in HMPSA formulation is a plasticizer and a viscosity-regulating agent.

The solvents for PSAs and the principles of their use (solvent–solute interaction according to the theory of solubility parameters and the Flory–Hildebrandt theory) were described in detail in Refs [15,46]. The choice of adequate solvents for various formulations (e.g., rubber–resin, acrylic, silicones, PURs), various tackifier resins, and different product classes (e.g., labels, tapes, and protection films) and solvent mixtures was discussed. The special role of solvents (e.g., cosolvents to improve wetting of water-based formulations, for thickeners, and for stabilizing of curing agents) was presented also. Solvents for printing inks were discussed and recycling of solvents was described. The role of the solvent for coating an image and for drying (running speed and residual solvent content) was discussed as well. Solvents for rubber–resin PSAs are discussed in Chapter 2.

8.2.4.2.2 Surface Active Agents

Surface active agents are used together with protective colloids in the off-line synthesis of PSA raw materials and in the formulation of PSAs to ensure coatability (wetting-out, low foam, shear stability, etc.) or improved solubility [15] (see also *Solubilizers*, Section 8.2.4.2.4). They may be polymerization (synthesis) related or postadditives. The surfactant level influences the solids content, free-monomer content, pH, surface tension, particle size, viscosity, chemical and mechanical stability, foaming, grit, water resistance, and transparency of the dispersion. Interaction of the surfactant with other layers in the laminate was discussed by Benedek in Ref. [46]. The surfactant may protect the adhesive during exposure to low temperatures. Generally, high surfactant concentrations lower the peel resistance and, in many cases, the shear resistance. The surfactant of the tackifier dispersions may be incompatible with the polymer, although the tackifier is miscible with the polymer [46]. The use of ethoxylated amines and polyalkylene oxides selected according to the HLB value for removable formulations was described by Czech in Ref. [28]. The surfactant affects water removability (see also Section 8.1.2.1.1). Surfactants influence the efficiency of light stabilizers and can lead to discoloration and bleeding (see also *Applications of Pressure-Sensitive Products*, Chapter 8).

Emulsifier monomers can also be included in the polymerization recipe. For instance, when COOH groups are not present in the polymer chain, SBRs are usually poststabilized with about 1–4% surfactants; antioxidants and pH-adjusting agents are also added. The influence of internal emulsifiers on removability was discussed in Ref. [27].

Wetting agents are technological additives used to allow or improve the wetting-out of the adhesive or other coating components on a solid-state carrier (face stock or release liner) [15]. Such surfactants are used in the synthesis of water-based dispersions

to ensure dispersion stability. They strongly influence the particle size and viscosity of the dispersion. The different surfactants used in connection with a particular colloid serve to enhance stability; modify surface tension, viscosity, and flow characteristics; and control the particle size of the resulting polymer emulsions. The wetting characteristics of the main substrate materials and surface tension of various water-based dispersions are listed by Benedek in Refs [15,46]. Special features of wetting, such as dynamic surface tension, HLB value, viscosity–surface tension interdependence by dilution value, and synergism of various surfactants were discussed. The working mechanism of various surfactants, the choice of surfactants, the main surfactant classes, and the technology of their use are described. The main sulfosuccinate and succinamate surfactants are listed. Wet-out improvement using blends of acetylenic diol, ethoxylate, and sulfosuccinate surfactants and the influence of fluorinated surfactants were described. The suggested wetting agent level was discussed in Ref. [13]. The influence of the surface active agent level on pH was investigated by Benedek in Ref. [46].

Defoamers are added to the dispersion to reduce foam formation. By lowering the surface tension, surfactants reduce the energy to create foam. There is no generally valid theory concerning the mechanism of defoamers. It is supposed that surfactants form a viscous film on the surface of aqueous solutions, in which bubbles of air can be encapsulated. In contrast, defoaming surfactants form a low-viscosity, mobile, open-surface film that forms areas of weakness in the surface of bubble, eventually leading to bubble rupture. Common defoaming agents (silicone derivatives or acetylenic alcohols) and other substances with a defoaming effect also (e.g., higher alcohols, oils, organic phosphates) are described in Ref. [41]. Foaming depends on the construction of the coating device also (see also Chapter 10). An excess of defoamers causes poor roll-to-roll adhesive transfer and pinholing [13]. Defoamers are discussed in detail by Foreman in Chapter 5.

8.2.4.2.3 Fillers

As discussed earlier (see Section 8.2.3), cohesion and certain special properties (e.g., removability, convertability) of PSAs can be improved by fillers. Fillers were described in detail in Refs [15,46]. In Ref. [46], fillers (pigments, extenders, and flameproof agents) for the whole domain of PSP components (i.e., liquid and solid-state components) were discussed. Fillers can be classified as reinforcing and special (e.g., neutralizing, crosslinking, conductive, flame retardant, pressure sensitive, water soluble, expandable) additives. The use of fillers and their influence on the modulus were described in detail in Ref. [15]. One method of raising resistance to cold flow is through the use of cohesive strengthening agents, such as calcium stearate, magnesium stearate, or ethyl cellulose. Typical optimal loadings are in the 10–20% range. The criteria for the choice of fillers (e.g., particle size and distribution, particle shape, density and bulk density, specific surface, hardness and abrasivity, oil absorption, pH value, and dispersion) and their suggested level for various PSAs (e.g., acrylics, rubber–resin, etc.) were also discussed. Special fillers are suggested for special performance characteristics like conductivity, cuttability, and solubility. The main fillers used for NR-based PSAs and their characteristics are discussed in detail in Chapter 2.

Conductive and flame-retardant fillers were described in detail in Ref. [15]. Conductive pressure-sensitive formulations are discussed in detail by Subramony in *Applications of Pressure-Sensitive Products,* Chapter 2.

Expandable and hollow filler particles were developed as well. Such fillers are used for foam-like products (see also *Applications of Pressure-Sensitive Products*, Chapters 1 and 7) and for UV-light-cured special tapes. Blends of PSAs with inherently tacky elastomeric microspheres or glass bubbles formulated for removable and repositionable PSAs were described in Ref. [28]. For instance, removable pressure-sensitive tapes containing resilient polymeric microspheres (20–66%), hollow thermoplastic expanded polymer (acrylo nitrile-vinylidene copolymer) spheres with a diameter of 10–125 μm, a density of 0.01–0.04 g/cm^3, and shell thickness of 0.02 μm in an isooctyl acrylate–acrylic acid copolymer, have been prepared. The particles are completely surrounded by the adhesive, with a thickness of at least 20 μm. When the adhesive is permanently bonded to the backing and the exposed surface has an irregular contour, a removable and repositionable product is obtained when the PSA forms a continuous matrix that is strippable bonded to the backing, with a thickness of greater than 1 mm.

The electrical properties of PSPs depend on the carrier. Agents improving the electrical and antistatic properties of plastic films can be added to the formulated raw materials during film manufacture or can be coated on the film. Electrically conductive PE (HDPE) is used for extrusion of tubes and film. Antistatic agents like polyethoxytiophene can be coated on the film surface. The electric performances of plastic films can be modified using radiation-induced cross-linking. For instance, a polyolefin film with an electrical resistance of 1600×10^{-2} Ohm has been manufactured through radiation-induced cross-linking. Conductive fillers improve the electrical conductivity and antistatic characteristics. Fillers for electrical conductivity are discussed in *Applications of Pressure-Sensitive Products*, Chapter 2. The most used filler to achieve enhanced electrical conductivity is carbon black. A level of 15–45% carbon black is suggested for use as filler. There is a logarithmic dependence between the electrical conductivity and concentration of carbon black.

Water as a filler must be taken into account in the formulation of pressure-sensitive hydrogels, where water can work as a plasticizer (see also Chapter 7), as an electrolyte in formulations for medical uses (see *Applications of Pressure-Sensitive Products*, Chapter 4), as an agent for regulation of the refractive index (see also *Applications of Pressure-Sensitive Products*, Chapter 3), etc.

8.2.4.2.4 Solubilizers

Solubilizers are additives that improve the water solubility/dispersibility of PSAs (see Section 8.1.2.1.1). As discussed in Ref. [15], such solubilizers can impart pressure sensitivity under well-defined conditions. Surfactants, protective colloids, monomers, water-soluble plastomers, fillers, tackifier resins, or plasticizers can work as solubilizers. Their function is based on the presence of polar functional groups, which allow the solvation of macromolecular compounds according to the thermodynamically determined mixing rules. Solubilizers were described in detail in Ref. [15]. The use of solubilizers for water-soluble acrylic formulations was discussed in Ref. [31]. Formulation for water-solubility was the subject of Section 8.1.2.1.1.

8.2.4.2.5 Rheologic Agents

Rheologic agents are used as pH or viscosity controllers, stabilizing agents, thickeners, or viscosity-reducing agents. The control of pH is of decisive importance for water-based formulations. Such control influences both the rheologic properties of the dispersed system and its chemical reactivity. The adjustment of the pH can modify the viscosity, solubility, stability, and adhesive properties of PSAs.

The control of pH is of decisive importance for water-based systems. pH influences both the rheologic properties of the dispersed system and its chemical reactivity. It can modify the viscosity, solubility, and adhesive properties of PSAs. Neutralization may change dispersion stability, adhesive, and end-use properties (e.g., tack, shear, water sensitivity, and aging resistance). The effect of neutralization is discussed in detail by Foreman in Chapter 5. Generally, water-based dispersions are stable above a pH of 2, acrylic dispersions are usually delivered with a pH of 5–6, VAc copolymers at a pH of 4–5, and NR and neoprene dispersions in the alkaline pH range [46]. To avoid ionic shock, formulation components must display the same pH range. Neutralization agents are discussed in Refs [15,46]. Nonvolatile neutralization agents may change the water absorption/desorption of polymer particles (i.e., drying properties) or interact with other components of the laminate. They also may change the viscosity or destroy ester-based surfactants. The modulus, peel resistance, and water resistance of the PSA depend on the nature of the neutralization agent used.

Thickeners can be used for viscosity regulation of water-based and solvent-based formulations (solutions or emulsions). Thickeners are discussed in detail by Foreman in Chapter 5. Increased viscosity can be required for better wetting-out or to avoid penetration. To be coatable on different machines, water-based PSAs must be thickened. For instance, when using CSBR latexes, it is better to produce a low-viscosity latex and control the final rheology of the adhesive through the addition of thickeners. An apparent thickening should be achieved using thickeners. Some surfactants also act as thickeners. The viscosity increase based on the polar interactions between the molecules can be easily reduced by shearing. Migration in paper can also be avoided using thickeners. Such rheologic additives can be divided into inorganic products, polyacrylic copolymers, cellulose derivatives, polysaccharides, polyethylene oxides, and associative thickeners such as PURs. Their working mechanism, choice, and formulating technology were discussed in detail in Refs [15,46]. Thickening power is influenced by the type of emulsifier, particle size, and mineral fillers. Plasticizers and solvents can produce thickening also.

Thickeners can increase water-sensitivity and act as nutrients for microorganisms. The thickener influences the adhesion to the substrate, the hardness of the film, its curing, blister formation, and corrosion properties. Thickening influences (reduces) the drying speed, decreases penetration to the paper, and, thus, indirectly increases the coating thickness. Generally, thickening reduces tack and improves wet tack. Common thickeners used for water-based PSAs were listed in Ref. [46]. The technology of thickening is also discussed in Ref. [15].

Certain technological additives are suggested for the reduction of viscosity of dissolved or dispersed systems. Such viscosity reducers are described in Refs [15,46], where their influence on the viscosity is discussed.

Protective colloids serve to stabilize polymer emulsion (see also Chapter 1). These are water-soluble hydrophilic compounds that are not absorbed within the polymer particles but function by coating the polymer particle, by raising the viscosity of the aqueous phase, or by other means to prevent polymer-to-polymer interactions leading to coagulation and agglomeration [15]. Such stabilizing agents were discussed by Benedek in Refs [15,46].

8.2.4.2.6 Other Technological Additives

Humidification agents, antimigration agents, and cuttability additives are used also. Stabilization of the water content of adhesives is carried out with special hygroscopic agents. Such humidification agents improve the hydrophilicity of the formulations [15]. Polyols and low-molecular-weight sugar derivatives, alone or together with carbamide, are used. Antimigration agents reduce the migration of low-molecular-weight substances by absorbing them or building up barrier layers. For water-based formulations, antimigration agents based on EVAc copolymers are used; for HMPSAs, ethylene copolymers are used [15]. Compounds that work as detackifiers (see also Section 8.2.1.4) or antimigration agents can avoid excessive adhesive flow and thus improve cuttability [15] (see also Section 8.1.5.2.1 and Chapter 10). Low-molecular-weight ethylene copolymers are suggested as cuttability additives. According to Merrill and Machielse [86], low-molecular-weight polyolefin polymers and copolymers can improve bond strength, wetting, and adhesion, modify permanent tack, and provide antiblock performance and rheology control. For instance, for a triblock SIS formulation based on Kraton 1161 (1107) (30%), C5 tackifier resin (49.5%), naphthenic process oil (19.5%), antioxidant 1%, the additive A-C® 400 13% VA EVA (3%) improves face stock penetration, aged probe tack, peel resistance (aged), and shear resistance (aged).

8.2.5 Formulation of Other Coating Components

As discussed in *Applications of Pressure-Sensitive Products*, Chapter 1, PSPs can include other nonadhesive coated layers, such as primers, antistatic agents, antifog agents, printing inks, and lacquers. Generally, such compounds are supplied ready to use by the chemical industry; thus, it is not the aim of this book to describe them. Some of these components, which are used in the manufacture of the carrier, were described in detail by Benedek in Ref. [46]. Printing inks were described in Ref. [46]. In this section only the primers will be presented because of their adhesive-related formulation.

Generally, primers form an intermediate layer between the carrier material and the adhesive. They are used to improve the anchorage of the adhesive (or of the release liner), to improve the quality of the adhesive layer, or as a release layer. Primers are recommended mainly for plastic film carriers. For instance, on untreated PE surfaces common acrylic PSAs exhibit a peel force of only 4 N/cm; to improve their anchorage, primers must be applied. Many difficult-to-adhere-to substrates exist, from which PSA tape backing is made. PET, polyimide (e.g., Kapton®), and polytetrafluoroethylene (e.g., Teflon®) substrates have historically required some type of preparation prior to silicone adhesive application and curing. Surface treatments include generating an oxide layer,

either chemically or by electrical or flame plasma, to allow silicone adhesives to bind tightly to the substrate (see also Chapter 10). Another method is to employ an intermediate primer coat of a composition that will bind the carrier and PSA together.

The application and mechanism of primer coating for direct and transfer coating is described in Ref. [48]. In direct coating the primer improves the anchorage (increases the chemical affinity; no smoothening effect is required), strengthens the face stock (reinforces the fiber structure, strengthens the surface layer), absorb stresses, stiffens the face stock material (changes the peel resistance and cuttability), limits adhesive bleedthrough, and influences drying. For transfer coating, the primer improves the anchorage (smooths the paper face stock, increases the chemical affinity), strengthens the face stock, absorbs stresses, and stiffens the face stock. The influence of the primer on removability was discussed by Benedek in Ref. [17]. As demonstrated, primer softness, structure, and geometry strongly affect removability.

The chemical nature of primers depends on the substrate to be coated and on the postcoated adhesive. Various products, like ABS, isocyanates, and silane derivatives, can be coated as primers. Titanate primers are also known to act as adhesion promoters for silicone gels by increasing the anchorage of the gel to a given substrate. A primer of industrial importance for silicone adhesives is essentially a polydimethylsiloxane in a solvent system. Organosilane-based primers were used by Kuroda [87] to chemically treat substrates. Kerr [88] described a phenyl-based primer offering the specific property required to bridge phenylsiloxane-based silicone PSAs and backing materials. Gantner et al. [89] created silicone gel formulations for medical devices, including a hydroxy-substituted siloxane resin that does not require priming or surface treatments of the backing substrate to achieve adequate adhesion. In some cases (e.g., protective films or tapes), primers are cross-linked versions of the base adhesive used to coat a carrier material (see also *Applications of Pressure-Sensitive Products*, Chapter 4). For instance, a primer for a polyethylene tape and based on butyl rubber consists essentially of a butyl rubber, a polyisocyanate, and an organic solvent. For silicone tapes with PE or PET carrier, a primer containing organosilicones, nitrile rubber, and polyterpene resin is recommended.

In other cases, polar, reactive elastomers are used as the main component for the primer. For instance, a blend of chlorinated rubber, EVAc copolymer, and chlorinated PP can be used as a primer for a polypropylene carrier. As a classic primer, solutions (in toluene) of butadiene acrylnitrile–styrene copolymers have been preferred. For PVC tapes coated with a chlorinated rubber, primers based on butadiene–acrylnitrile rubber and butadiene–styrene rubber (1:1), with a butadiene/styrene ratio of 1/8, have been proposed. For such products, the primer layer has a thickness of 2–6 g/m^2. For solvent-sensitive SPVC films, primer dispersions based on Hycar Latex and Acronal 500 D (1/1) have been suggested. The effect of primers depends on the coating weight and coating conditions. Theoretically, primer thicknesses approaching a single molecular layer are required, but in reality the primer coating is 0.5–1.0 μm thick.

Polar ethylene copolymers are suggested as adhesion promoters also. Ethylene–acrylic acid copolymers (EAA) with randomly distributed carboxy groups provide excellent adhesion characteristics when bonding with polar surfaces. In such copolymers, the carboxyl groups disrupt crystallinity and also provide a site for hydrogen bonding between

molecules. EAA polymers are applied mainly to prime foil (0.5–1.0 lb/3000 ft^2), but they can be used on paper as well and are also supplied as water-borne dispersions.

Generally, water-based primers are used for paper and solvent-based primers are used for films. Water-penetrable carrier materials are primed with water-based solutions of resins or latex. A release coating may also need a primer. For instance, a barrier layer based on vinyl chloride, vinyl acetate, and vinyl alcohol is applied to paper before siliconization.

A discontinuous adhesive layer can be preprimed to provide a continuous matrix. As discussed earlier, the PSA surface can have a special discontinuous shape ensured by the PSA itself if it is a suspension polymer. Thus, spherical contact sites are formed that are anchored on the carrier surface with the aid of a primer.

Formulation of primers as a function of the PSP class, carrier material, PSA, and coating method was discussed in Refs [16,46]. In Ref. [16], screening formulations are also given. Primers for extruded layers are discussed in Ref. [46]. Such primers are used in carrier manufacture and in the manufacture of adhesiveless, self-adhesive products.

On tapes with impregnated paper carrier, butadiene–styrene rubber may function as an abhesion promoter. For instance, a primer based on SBR latex is coated on the carrier for removable PSAs.

8.3 Progress in the Formulation of Pressure-Sensitive Adhesives

Upon examination of the progress in the formulation of PSAs, it is clear there is a need to differentiate between improved products in the well-known domain of classic raw materials for PSAs (i.e., elastomers, viscoelastomers, or additives) and approaches based on new raw materials. One class of new raw materials used for PSPs is plastics, formulated through simultaneous cross-linking–tackifying.

8.3.1 Plastics-Based Pressure-Sensitive Adhesives

Some years ago, a new class of PSAs was developed based on water-soluble plastics [6,34]. In a different manner from common PSAs, such formulations possess a wet tack and good adhesion to aqueous (humid) surfaces (e.g., to biopolymers). The first formulations were based on PVP and a PEG [90–92]. In such formulations, simultaneous cross-linking/plasticizing occurs. Rubber-like elasticity and pressure-sensitive adhesion of such compounds are due to the formation of an interpolymer hydrogen bonded complex. The cross-linking acts via hydrogen bonding of the carbonyl groups of PVP through the OH end groups of the polyglycol. This polymer is water soluble and possesses pressure sensitivity.

The use of PVP as a solubilizer for water-soluble PSA formulations has been practiced for many years, and recipes using both (i.e., the water-soluble plastics and the water-soluble oligomer) were known as well [43]. Recently, HyunSung Do et al. [39] prepared and characterized water-soluble acrylic PSAs that contain PEG to improve water solubility. Moreover, according to the patents listed in Ref. [43], the ratio of the components

is critical for the detackifying effect of such additives in common pressure-sensitive formulations. However, the possibility of using such components as main constituents for PSAs (i.e., as viscoelastomer) was discovered and forced by Feldstein et al. [6,34].

Later, the low functional and long-chain cross-linkers (called *carcass-like cross-linkers*) were used together with multifunctional cross-linkers (called *ladder-like cross-linkers*), giving rise to pressure-sensitive hydrogels, which combine tack typical of conventional hydrophobic PSAs with the capability to adhere to highly hydrated substrates, which is typical of bioadhesives. Water as a plasticizer was incorporated in the formulations as well. The adhesive behavior, mechanical properties, and water-absorbing capacity of such formulations are functions of the blend composition. The term "interpolymer complex" refers to the association of complementary polymers resulting from favorable interactions between their respective reactive groups. When the complementary polymers contain reactive functional groups in the repeating units of their backbones, the resulting complex has a so-called "ladder-like" structure. Owing to entropic reasons, the functional groups react in a cooperative manner forming sequences of relatively short and tough intermacromolecular bonds. The schematic structure of such s complex resembles a ladder. This ladder-like type of interpolymer acid–base complex was first described by Kabanov and Zezin [93]. The cooperative mechanism of the reactions of neutralization and exchange between macromolecules of polybases and polyacids, bearing reactive groups in their repeating units, implies that the process of polycomplex formation follows the principle "either all or nothing" and resembles fastening a zipper [94]. In turn, this type of polyelectrolyte complex formation leads to cohesively tough intermolecular structures, which exhibit a lack of significant free volume. However, pressure-sensitive adhesion is a specific balance between high cohesive strength and relatively large free volume. Addition of the appropriate plasticizer leads to increased free volume within the interpolymer complex. Mixing the FFP with LLC in a ratio of [FFP]:[LLC] = 10:1 led to dramatic increase in the value of ultimate tensile stress (by 6.6 times), whereas the value of maximum elongation at break decreased by a factor of 4.3. The former value may be regarded as an indirect measure of the cohesive strength of material, whereas the latter may be related to the free volume [6].

Common PSAs are based on elastomers or viscoelastomers. The elastomers are tackified, where the mobility of the macromolecular structure is enhanced by the tackifier or plasticizer. In formulations using viscoelastomers (e.g., acrylics, ethylene copolymers), tackification and plasticizing are not necessary, but possible; in such formulations, cross-linking is practiced. As noted above, a new formulation method has been developed based on a plastomer that is cross-linked and plasticized simultaneously [6,34]. In such formulations, water acts as a plasticizer too; thus, it works as a supplemental control parameter of the macromolecular construction. Moreover, in such a formulation neutralization of the LLC is also possible. Thus, it also functions as a control parameter of the polymer structure and pressure-sensitive properties. A similar influence of pH can be observed in biopolymers.

As discussed above, increased cohesion can be achieved by cross-linking the macromolecular structure and increased mobility by diluting the chains (plasticizing). Generally, different compounds are used for cross-linking and plasticizing. For the new hydrophilic PSAs, the simultaneous use of cross-linker and of plasticizers (i.e., of the

same cross-linker–plasticizer compound) is possible. Owing to their hydrophilic character and biocompatibility, such adhesives are very important in the application practice of drug delivery [34]. From the theoretical point of view, the main importance of the new class of PSAs became evident after "generalizing" such compositions (i.e., after the design of other "plastomer-based" PSAs), demonstrating that pressure sensitivity is based on molecular characteristics [6]. This enabled the statement of new criteria for pressure sensitivity [6,7].

8.3.2 Advances in Elastomers

Advances in the synthesis of new elastomers and their formulation are related to the development of classic preparative macromolecular chemistry, where new methods like atom transfer radical polymerization (ATRP) made possible the manufacture of block copolymers.

Advances in TPEs include the development of new synthesis methods and new monomers and perfecting of the classic synthesis of block copolymers. Although styrene is polymerizable using cationic, anionic, or free radical polymerization, for a long time anionic living polymerization has been considered the sole possible method for the synthesis of styrene block copolymers [95]. Later (1984), cationic copolymerization was developed for the synthesis of thermoplastic elastomers [96]. Polar, sequenced copolymers (block copolymers also), based on acrylates, styrene, and dienes, were synthesized using homogeneous metallocene catalysts as well, many years ago (1970), by Benedek et al. [97–99]. However, the "old" anionic copolymerization is the industrial polymerization method for commercial styrene block copolymers. Although special monomers were synthesized also (the main problem is the adequate bulky component), economic considerations impose the use of styrene as a hard component in such block copolymers. Thus, industrial efforts were focused on perfecting the sequential anionic copolymerization of styrene and dienes. In the range of new products, acrylic TPEs have been developed (see also Chapter 3).

Substantial benefits could also be realized by developing PSAs from acrylic block copolymers [100]; therefore, such copolymers have received recent attention for potential use as HMPSAs [101–105]. Numerous firms have explored methods to synthesize acrylic block copolymers by free radical and ionic processes. Early free radical synthesis incorporated Pst [106] and polyacrylate macromers to form comb-like block copolymers. These [107] were limited in molecular weight of the hard blocks to a few thousand Da. More recent works involved multivalent chain transfer agents [108] and living radical polymerization [107,109]. Anionic methods have the advantage [110] of better control of polymer architecture and tacticity [111,112]. However, little work on acrylic block copolymers such as PSAs has been published. Such copolymers are not "new." Some decades ago, acrylic block copolymers were synthesized but their high molecular weight led to excessive viscosities. The methods of synthesis and the structure of the polymers were improved. Advances in the processability of acrylic-based HMPSAs are described by Hu and Paul in Chapter 3.

Recently, Yamamoto and coworkers [113] synthesized poly(AA)-b-polybutylacrylate-b-poly(AA) (PAA-b-PBA-b-PAA) triblock copolymers and reported bulk viscoelastic

characteristics and "holding power" of films. Chen and Shull [114] demonstrate that triblock copolymers with PEG acrylate midblocks could be used in an aqueous environment. Drzal and Shull [115] studied the adhesive failure criteria in PSAs of anionically polymerized polymethyl methacrylate-b-poly(*n*-butylacrylate)-polymethyl methacrylate (PMMA-b-PnBA-b-PMMA).

Acrylic block copolymers were studied by M. Guvendiren et al. [116]. PMMA-tert-butyl methacrylate-methyl methacrylate) (PMMA-PtBMA-PMMA) triblock copolymer was synthesized by anionic polymerization, followed by conversion of the midblock into a methacrylic acid PMMA-PtBMA-PMMA triblock copolymer.

Well-defined acrylic block copolymer materials for model PSAs have been synthesized using ATRP [117]. Diblock and triblock copolymers of PMMA and poly(*n*-butyl acrylate) (PnBA) have been synthesized by controlled radical polymerization. PMMA and PBA macroinitiators for creating PMMA-b-PnBA diblock copolymers and PMMA-b-PBA-b-PMMA triblock copolymers were synthesized. Tack measurements demonstrate that blending these block copolymers with a homopolymer of the midblock polymer can be used, to some extent, to tailor the tack to values that are better than the values for the neat block copolymers, but still within the range that can be studied with scanning probe techniques with modified tips.

Smit et al. [78] investigated anionically synthesized block copolymers with MMA hard blocks and a BA soft mid-block. Such polymers have a lower M_e for mid-block and higher end-block T_g (130°C for MMA vs 100°C for atactic styrene in common SBCs). One disadvantage of styrenic block copolymers is that the entanglement molecular weight (M_e) of the end-block (styrene) is quite high (18 kDa). Thus, obtaining the full T_g of the end-block copolymer requires either higher overall molecular weight or high styrene content. The low M_e of MMA (4.7 kDa) loosens this constraint. In addition, the BA mid-block has much higher M_e (17 kDa) vs isoprene (7 k) or butadiene (1.7 kDa) or their hydrogenated counterparts (about 1.7 kDa). Thus, maintaining stiffness below the Dahlquist criterion of 3×10^6 dyn/cm is easier, and higher level of polymer can be used. The acrylic polymer is much softer, possesses a lower plateau modulus, is more heat resistant, and has a higher hard block T_g. The SIS demonstrates a T_g of about 100°C, followed by an order/disorder transition at about 140°C, whereas the acrylic T_g appears at 120–130°C. Simal et al. [76] investigated the properties and formulation of a novel four-arm radial block copolymer (A-B)4 obtained using ATRP (see also Chapters 3 and 5).

8.3.3 Advances in Cross-Linking

The temperature-dependent cohesion of SBCs was improved by chemical cross-linking. For instance, Lim et al. [118] studied the adhesion performance and viscoelastic properties of UV-cross-linked SBS-based HMPSAs using chemical cross-linking by photoinduced addition of a thiol group (RSH) onto an olefinic double bond of the base polymer. The thiol-ene reaction is less affected by air inhibition, because peroxide radicals formed by the O_2 scavenging of alkyl radicals are also removed from the hydrogen atoms of thiol. Trimethylolpropane mercaptopropionate as photocross-linker is an effective cross-linker for the SBS-based polymers.

Cashiona et al. [119] prepared PSAs demonstrating a synergy of hydrogen bonding and photocross-linkable sites. Hydrogen bonding is a versatile scaffold for noncovalent associations due to the fact that hydrogen bonding functionality is prevalent in biological systems (see hydrogels), it is readily accessible, and the associations are reversible. Photocuring-associated macromolecular architecture is a relatively unexplored theme that has received significant interest in the layer-by-layer assembly of multilayer thin films [120] formation of supramolecular nanostructures [121] and formation of liquid crystalline polymers [122]. Cross-linking of hydrogen-bonded acrylic architectures to increase the cohesive strength of low-molecular-weight HMPSAs has received little attention. The functionalization of acrylic copolymers with urethane and cinnamate functionalities introduces a novel combination of hydrogen bonding and UV-curable substituents, respectively. The photochemistry of cinnamates involves two photoreactions upon UV irradiation (i.e., the *trans–cis* isomerization and photodimerization) [123]. Precursor copolymers were functionalized with various degrees of hydrogen bonding and UV-curable moieties. The hydroxyl group of HEA was reacted with cyclohexyl isocyanate and cinnamoyl chloride to provide urethane and cinnamate functionalities, respectively. Higher molar ratios of urethane increased peel values through coupling of hydrogen bonding.

A glycidyl methacrylate monomer containing both acrylic and epoxy groups can be copolymerized with an acrylic or vinyl group containing monomers and provides a epoxy ring functionality with an acrylic polymer backbone. By varying other acrylic monomers, the physical and chemical properties of copolymers can be changed. Because these copolymers contain an epoxy group, the cross-linking reaction can occur with amines, carboxylic acids, anhydrides, and hydroxyl groups containing polymers. In general, these cross-linking reactions proceed in an elevated temperature condition. In the cross-linking reaction, the ring-opening reaction of the epoxy group yields secondary alcohols. However, in the case of the cross-linking reaction of the epoxy group with carboxylic acids and anhydrides, the generated hydroxyl group can react with acids to ester reaction at high temperature (over 130°C). These second reactions (ester reaction) can make cross-linking density more dense [124].

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9

Silicone Release Coating Technology

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Randall G. Schmidt
Dow Corning Corporation

9.1 Introduction

Release coatings are generally used to prevent things from sticking together. This simplistic statement embraces a wealth of technology and a global industry involving both silicone and nonsilicone materials. At their simplest level, fluids or powders are coated or sprayed onto a surface to provide a nonstick surface for another material subsequently brought into contact with it. This type of release agent is *nonpermanent* and usually results in significant transfer of release agent to the released surface. This transfer is called migration or offset. Migratory coatings include soaps, oils, fluorocarbons, silicone oils, and even, under the right circumstances, water (humidification of large-surface, film-based decals is a common way to allow their repositionability during application). They are effective because they form a weak boundary between the two surfaces and result in release agent being lost from the original treated surface, such as a mold, and being transferred to the released surface as surface contamination. These materials are not used for pressure-sensitive release.

Semipermanent release coatings form a somewhat more sophisticated set of materials. These result in some transfer to the released surface, but in a much smaller proportion. The release agent itself is not usually a simple fluid, but instead is a compounded material involving solid materials dispersed in fluids or oils. Semipermanent coatings include wax dispersions, mixtures of silicone resins and silicone fluids, micas in various fluids, and organic resins such as acrylics (some "detackification agents" are based on such compositions; see also Chapter 8).

Temporary and semipermanent coatings are mentioned only to highlight the specialized nature of our subject, which is essentially *nonmigratory* coatings that are permanent (or at least capable of multiple uses) and have excellent antistick properties. These applications are dominated by silicones. However, some organic materials, such as urethanes, fluorocarbons, carbamates, vinyl acetate copolymers and acrylics, can be used when either the toughness of the release surface or the absence of silicone is of greater importance than absolute ease of release. In this chapter, we are concerned only with silicone release coatings. Silicones in many forms offer excellent release properties, but to present a nonstick surface and, at the same time, offer little or no transfer to the released surface, a cured filmic surface free from migratory species is required. This presents many challenges and involves the use of cross-linking or curing chemistry to provide "cured" silicone release coatings. Owing to the somewhat complex and multistep operations involved in the manufacture of pressure-sensitive labels and other constructions, "release" is not as simple as "being able to separate two materials." The ability to control the actual force required and the knowledge to accomplish it will be discussed in this chapter. As with other multistep operations, many other aspects of performance come into play beside release; they will also be discussed.

9.2 Components of Silicone Release Systems

9.2.1 Cure Chemistry

As mentioned in the Introduction, a curable silicone composition must be used for pressure-sensitive applications to minimize the potential of contaminating the adhesive surface resulting in reduced tack and adhesion. A number of cure chemistries have been employed, almost all of which are still in use today to varying degrees. The chemistry has evolved because of changing processing, regulatory, economic, and performance needs, sometimes based also on the evolution of adhesives and substrates used in pressure-sensitive applications.

Before embarking on a discussion of cure chemistry, some attention to what is meant by "cure" is necessary. The state of cure of a silicone coating can be measured in several ways. Because the function of a release coating is to deliver the adhesive to its final use, the ultimate test is what is acceptable in the end-use application without impairing adhesive performance. The most obvious impairment modes are loss of adhesive tack due to silicone transfer and, conversely, the inability to remove the release liner due to the reaction between the silicone and the adhesive. If the end use is a pressure-sensitive labeling application, both result in the inability to attach a label to a package or item (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Most forms of silicones for these applications are oily in nature (once any diluent is removed) and progressively cure into a solid silicone rubber as a cross-linking reaction

takes place. The appearance of cure means the surface is no longer oily, and no oily material can transfer to anything put in contact with it. Thus, the state-of-the art measure of cure is an extraction test with organic solvent. The amount of silicone extracted from the coating is desired to be, in most cases, less than 5% and in some cases less than 3%. It has been somewhat impractical to achieve less than 2% extractable silicone. In many cases, the amount of extractable silicone has also been correlated with some other measure of silicone transfer such as a qualitative tape test, a quantitative dye spreading/wetting test, a more sophisticated (and expensive) surface measurement, Electron Spectroscopy for Chemical Analysis (ESCA), or another performance test such as subsequent adhesion or tack. Other methods to compare the cure rates of coating formulations exist, but those mentioned above are the ones most commonly used and more easily performed on a coated surface in a production setting.

The basic functional component of a silicone release coating is a polydimethylsiloxane (PDMS) polymer (Figure 9.1). To provide a curable composition, various functional groups are substituted for some of the methyl groups. Maximum release performance, however, is obtained from maximizing the dimethyl content of the cured coating. Therein lies a never-ending conflict between speed of cure, which is maximized by a high concentration of functional groups and catalysts, and release performance, which is enhanced by a maximum concentration of dimethyl siloxane groups.

The following cure chemistries have been utilized in release coating compositions.

A. $Si–OH + SiH \rightarrow Si–O–Si + H_2$
B. $Si–OH + Si\text{-}OH \rightarrow Si–O–Si + HOH$
C. $Si–OH + Si\text{-}OR \rightarrow Si–O–Si + ROH$
D. $2Si–OR + 2HOH \rightarrow 2Si–OH + 2ROH \rightarrow Si–O–Si + HOH$
E. $Si–CH{=}CH_2 + SiH \rightarrow Si–CH_2–CH_2–Si$
F. Electron beam (EB) cure of silicone acrylate (see Figure 9.5)
G. Ultraviolet (UV) cure (see Figure 9.6)

9.2.1.1 Condensation Cure

Examples A through D are employed in what is generally referred to as "condensation cure." Example A is the primary cross-linking mechanism, whereas example B is the secondary but still very prevalent and critical condensation reaction. C and D are additional reactions that take place with the addition of materials known as fast-cure additives.

One advantage of this chemistry is that it is very fast when a suitable catalyst is used. It is also inexpensive and easily made into polymers. This chemistry is not susceptible to poisoning, so it is unaffected by potential substrate inhibition. One disadvantage is the great difficulty in putting the SiOH anywhere except on the terminal silicone atoms of polymers. In addition, this system needs a catalyst, normally an organotin salt, at levels

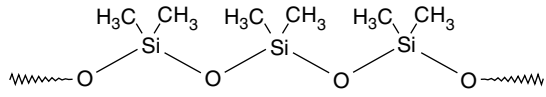


FIGURE 9.1 PDMS polymer structure.

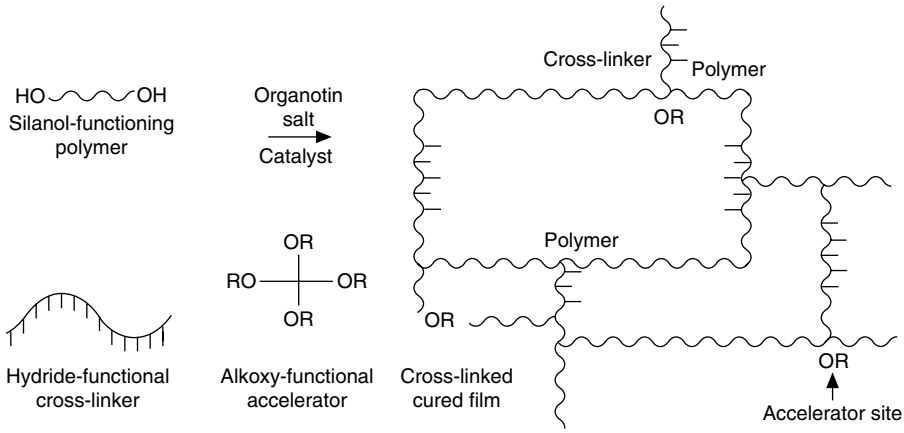


FIGURE 9.2 Tin-catalyzed condensation cure system schematic.

of 2 to 15% by weight. Because the catalyst is not easily poisoned, it is very difficult to control bath or working life once catalyzed. Because of its high reactivity, even at room temperature, this chemistry can be utilized only when diluted in a solvent or made into a reactive emulsion system.

The schematic for this system is illustrated in Figure 9.2. These coatings were the basis of the silicone release liner business from the late 1950s until the mid 1970s.

With this chemistry, control of release performance, which will be discussed in more detail later, involves controlling the elasticity, or cross-link density, of the cured silicone film. This is easily achieved by controlling the chain length of the polymer. Polymers ranging from 20 to 5000 siloxane units are employed.

The advantages are fast, low-temperature cure, a relatively wide range of release available through polymer molecular weight control, and freedom from substrate inhibition. The disadvantages are somewhat lengthier. There is no 100% solids alternative; indeed, even in solvent it is difficult to operate much above 8% solids. The reversible nature of this chemistry (Reaction B) leads to a phenomenon called blocking, in which liner coated with silicone on both sides tends to bond to itself during storage. Migration tends to be more prevalent with this chemistry as well (see also *Applications of Pressure-Sensitive Products*, Chapter 8).

9.2.1.2 Addition Cure

The most dominant cure chemistry used today involves example E, known as "addition cure," which is depicted in Figure 9.3. A silicone hydride group is added across a vinyl group, and nothing is evolved during cure. In the presence of the catalyst, the addition goes very rapidly with the evolution of heat. This chemistry has been formulated into 100% silicone solids, solvent-diluted, and emulsion systems.

In dilute solution, the bath life can be controlled much as in the condensation system, but for high solids or 100% solids, selective inhibition must be used. Commonly used inhibitors effectively exclude the vinyl groups from the platinum at temperatures around

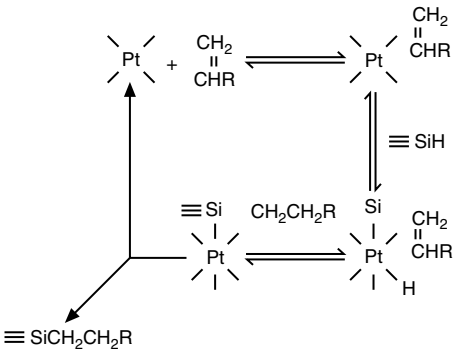


FIGURE 9.3 Addition-cure mechanism.

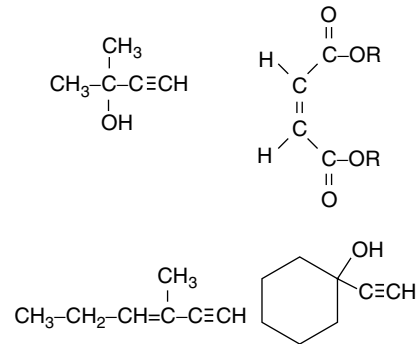


FIGURE 9.4 Inhibitor examples.

room temperature. At elevated temperatures above 80°C, these inhibitors evaporate, dissociate from the platinum, or react with the SiH and become part of the cured matrix. In either case, they can no longer exclude the polymer vinyl groups, and cure takes place rapidly. Such inhibitors include various acetylenic alcohols, materials containing double and triple carbon–carbon bonds, various unsaturated dicarboxylic acid esters, and some ketoximes (see Figure 9.4.) Materials such as amines, sulfides, phosphides, and the organotin salts used as catalysts in the condensation system form somewhat stronger bonds with the platinum and are generally referred to as poisons. Their presence makes it difficult, if not impossible, to cure an addition-curing coating.

A highly advantageous feature of this chemistry is the ease of polymer manufacture. Whereas silanol groups are only easily placed terminally, vinyl groups may be placed not only terminally but also anywhere along the polymer chain, as desired. Furthermore, these polymers will stand heat treatment better than silanol-functional polymers and so are more easily devolatilized to remove lower-molecular-weight species. This further aids the cause of migration-free coatings.

Thus, in addition to the ability to control the elasticity of the cured film by polymer chain length is the scope to do so by manipulating both the number and the distribution of vinyl groups along the chain.

The chemistry has no reversible reactions in the mechanism and so is free from the blocking phenomenon discussed previously. The major disadvantage is the sensitivity to poisoning either by the substrate being coated or by the introduction of foreign material prior to coating.

9.2.1.3 Radiation Cure

Although they were available in limited fashion in the 1980s, radiation-curing silicone release systems received more attention in the 1990s. Several key developments were made, and both EB- and UV-cured systems were commercialized (Figures 9.5 and 9.6). In these systems, the siloxane polymer also has methyl groups replaced by functional groups that will participate in cross-linking reactions. Example F is typically made practical by substitution with acrylate groups and exposure to a high-energy EB to create radicals. These radicals are, by nature, unstable and must combine with other radicals

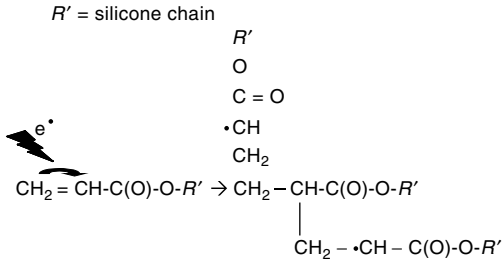


FIGURE 9.5 EB cure of silicone acrylate.

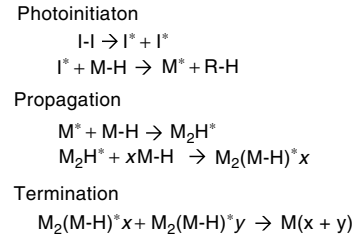


FIGURE 9.6 UV curing mechanism.

to satisfy their need for electrons. During this search for stability, the radicals are propagated to many other available reactive groups.

Example G is generally accomplished with a ring-opening epoxy group, facilitated by a catalyst that absorbs a certain frequency of UV energy. The higher concentration of reactive groups facilitates the speed of the reaction and sets the cross-link density. As mentioned previously, however, the greater substitution of functional groups for methyl groups compromises release performance, and these systems have not provided the range of release performance available from thermally cured systems.

Both EB and UV chemistries have the advantage of complete cure at relatively low temperatures. This makes them eminently suitable for temperature-sensitive substrates. Whereas the acrylate systems can be used on most papers, they do require inerting with nitrogen. The UV cure systems commercialized to date have all required the development of special papers, which has limited their general use.

9.2.2 Formulating

9.2.2.1 Condensation-Cured Materials

Basic polymers (see Figure 9.7)
Cross-linkers (see Figure 9.8)
Catalysts (see Figure 9.9)
Fast-cure additives: $Si(OR)_4$,
where *R* is of a type such as $CH_2CH_2OCH_3$, etc.
Anchorage additives: epoxy-functional materials
High-release additives: resin-based of the *M:Q* resin type (see Section 9.3.2.2 and Chapter 6)

The selections made will reflect the desired release performance. The basic polymers range from low-viscosity fluids, where $n \sim 20$, to thick gums, where $n \sim 6{,}000$. Blending various molecular weight materials permits variation in cross-link density, thus allowing release force control. Cure rates differ as the molecular weight ranges, but all will cure at room temperature after solvent removal. To enable cure in a release liner production setting, however, the silicone-coated substrate is exposed to hot air. Catalyst choice

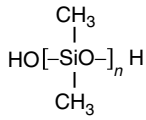


FIGURE 9.7 Basic siloxane polymers for condensation cure where *n* ranges from ~20 to ~6,000.

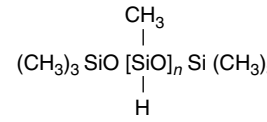


FIGURE 9.8 Cross-linker for condensation cure where $n \sim 40$.

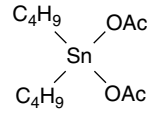


FIGURE 9.9 Typical catalyst for condensation cure where OAc can be laurate, hexanoate, acetate, etc., such as dibutyl tin diacetate or dibutyl tin di-2-ethylhexanoate.

will be a reflection of solvent choice, oven temperatures, and regulatory status. Anchorage additives are occasionally necessary on some substrates.

In emulsion form, the lower-molecular-weight polymers can be mechanically emulsified, as can the more hydrolytically stable catalysts. Emulsion systems do not have fast-cure additives or good high-release additives, but often do not need them. Water-soluble organics such as polyvinyl alcohol, carboxymethyl cellulose, starch, and others can be used with these systems to allow them to be used on more porous substrates and to affect release.

9.2.2.2 Addition-Cured Materials

Basic polymers (see Figure 9.10).

In solvent products, high-molecular-weight gums are used. Solventless and emulsion products use much lower-molecular-weight materials, as depicted in Figure 9.11, which are required by the application methods.

Cross-linkers: both homo- and copolymers of SiH functionality are used (see Figure 9.12).

Homopolymers are chosen primarily for their rapid gelation and improved anchorage. Copolymers offer better bath life and faster cure. Blends of homopolymers and copolymers are often used to optimize a balance between cure rate and anchorage.

Catalysts: Noble metal organo complexes are used. To improve solubility in 100% silicone systems, they are usually platinum or rhodium organosilicone complexes. The normal level is 50 to 150 ppm platinum metal, based on total silicone content, although recent developments have allowed platinum levels to be reduced to as low as 20 ppm.

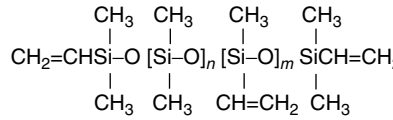


FIGURE 9.10 Typical silicone polymers for addition cure where $n + m$ ranges from 100 to 5,000 and $n/(n + m) = 0.96–1.0$.

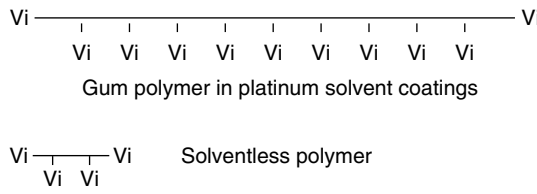


FIGURE 9.11 Relative structures of gum polymer and solventless polymer.

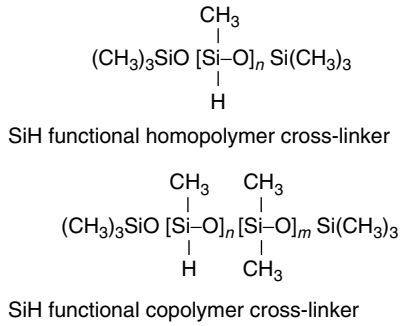


FIGURE 9.12 SiH addition-cure cross-linker types.

Inhibitors: Inhibitors were listed under the chemistry section. The selection of inhibitor impacts a number of cure and coating characteristics, some surprisingly. Inhibitors usually range from strong inhibitors with long, stable control on bath life but higher initiation temperatures to weak inhibitors with lower initiation temperatures and shorter bath lives.

High-release additives: These are essentially the same kinds of resinous materials used in condensation systems, but with the added advantage of being functionalized to enable cure into the network. Because they are solids, soluble (and produced) in hydrocarbon solvents, their use in solvent-based materials is straightforward. For emulsions and solventless materials, however, they must be dispersed in silicone polymer. This automatically limits the amount of resin that can be incorporated into a coating, because the polymer is added simultaneously.

If the resin content is too high in solventless systems, coating problems arise because the viscosity rises rapidly with resin content. Studies of resin molecular weight, type, and

functionality have demonstrated some impact on the efficiency of raising release, but the significance is minor compared with the effect of resin concentration. The efficacy of high-release additives is a major concern in both emulsion and solventless areas. A variety of materials are available that use different diluents, including organics, to control viscosity, and these diluents also have an impact on release. More details can be found in Section 9.3.2.1.2.

9.2.2.3 How Formulation Components Impact Processing and Performance

Each of these components has an impact on more than one aspect of the processing and performance of a silicone release coating. A summary is presented in Table 9.1, specifically with respect to their impact in solventless release coatings.

Because release is the main function of these materials and the polymer has the greatest impact on release performance, it is naturally the component selected first. The impact of polymer architecture on release performance will be further discussed in the next section. The current section will deal with the other aspects of performance, such as cure, bath life, and anchorage.

Solventless polymers can range in viscosity from 200 Pa · s to 2,000 Pa · s. For practical coating purposes, however, typical polymer viscosities range from 200 to 700 Pa · s. The general classification of polymers is end-blocked only, multifunctional, pendant only, and branched (see Figure 9.13). Terminal vinyl is more reactive than pendant vinyl. When both types of vinyl are present on a polymer, the polymer has many more opportunities to react. A multifunctional polymer ties into the network and builds molecular weight faster than an end-blocked-only polymer. The branched polymers essentially utilize terminal-functional vinyl and, as such, are very reactive and build molecular weight

TABLE 9.1 Components of Solventless Release Coatings and Their Roles

Release Coating Components	Roles
Base polymer	Polymer architecture • Affects release values and release profile versus delamination speed • Affects release *stability* and general inertness of coating
Catalyst	Platinum level • Affects cure rate, bath life
Inhibitor	Chemistry • Affects bath life, cure rate, anchorage, and coatability
Cross-linker	Architecture and functionality • Affects anchorage, bath life, and cure rate
Release modifier	Architecture and diluent • Changes release values • Affects anchorage, bath life, and cure rate
Process aids and additives	Mist reduction • Effective at line speeds up to at least 3,500 fpm Anchorage • Can affect adhesive compatibililty and release stability

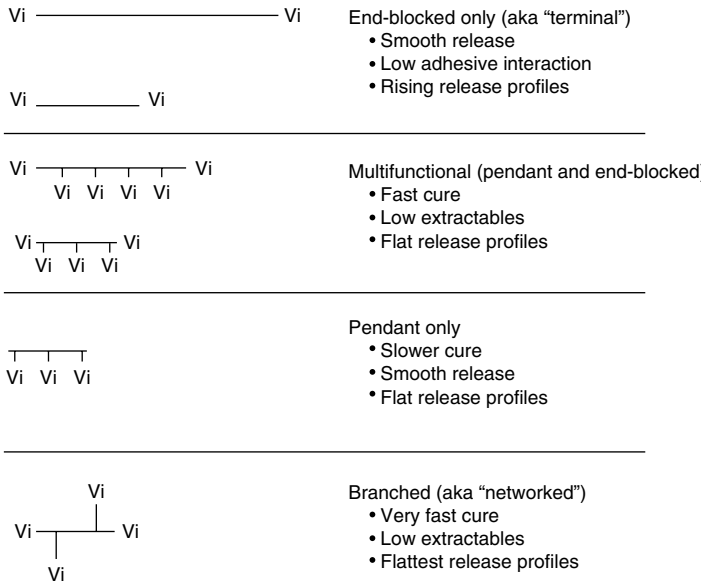


FIGURE 9.13 Addition-cure solventless polymer types. Vi = vinyl group ($CH{=}CH_2$)

more quickly. These polymers have allowed recently developed formulations to use lower than the traditional 100-ppm platinum catalyst to achieve the same state of cure.

From the same standpoint then, faster-reacting polymers tend to lead to shorter working bath life of a formulated coating, although this can be moderated to some extent with the choice and level of inhibitor. It is also generally observed that polymers that cure faster and lead to more highly cross-linked networks can pose more difficulty in achieving coverage of, and anchorage, to some substrates. Pendant-only polymers have special uses only for achieving certain release profiles because they tend to exhibit slower cure. For special substrates such as polyester and lower-temperature-resistant polyolefin films, additional polymer structure modifications have been necessary.

Once the polymer selection is made based on the release requirements, other formulation variables can be chosen to accommodate adhesive interaction, substrate compatibility, and processing requirements. The catalyst used for solventless silicone coatings is predominantly platinum. Rhodium catalyst has some niche applications that make it most suitable for combination with reactive, solvent-based acrylic adhesives. The rhodium complex, however, requires higher-temperature activation and as such is not suitable for use with most plastic substrates. Although it is somewhat obvious that the level of platinum catalyst affects cure and bath life, it is perhaps not so obvious that it can also play a role in coverage and anchorage.

The role of the inhibitor in the formulation is to provide a stable bath or working life to a coating until it is applied to the substrate and to allow cure to take place at the desired temperature and dwell time. This is depicted in Figure 9.14.

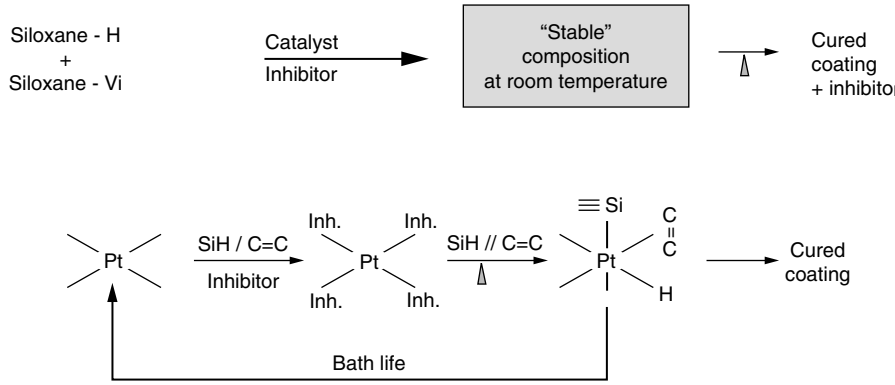


FIGURE 9.14 Role of inhibitor in addition-cure chemistry.

TABLE 9.2 Comparison of Inhibitors

	Inhibitor Comparison	
Performance Attribute	Acetylenic Alcohols	Maleates
Thin-film bath life	Poor/good	Excellent
Bulk bath life	Excellent	Poor/good
Coverage versus coat weight	Okay	Better
Low-temperature cure rate	Good/fair	Poor
Cure rate versus bath age	Poor/good	Excellent
Anchorage	Poor/good	Generally better

The requirements of an inhibitor come into play in the coating bath, on the application equipment, and once the coating is applied to the substrate. If the inhibitor forms a weak complex with the platinum, meaning a low-energy threshold will break the complex and allow low-temperature cure, then bath life can sometimes be extended by using a higher level of inhibitor. If an inhibitor is volatile and can leave the coating bath, a higher level of inhibitor is also often required. It is important for the coating to have a stable bulk viscosity so conditions for operating the application equipment remain consistent during use.

For solventless coatings, which are applied via roll coaters (see also Chapter 10), the coating must also remain uncured in the form of a thin film while it is transferred from one roll to the next. Once the coating is applied to the substrate, it needs to flow out, or level, over the irregularities of the substrate (especially important for paper) prior to gelation. Because the inhibitor affects speed of cure, it also impacts anchorage to the substrate.

Various chemical species were listed in the section on inhibitors, but the two general classes of chemicals most commonly in use are acetylenic alcohols and maleates. These are compared for their performance attributes in Table 9.2, which provides a general property comparison. The range of performance within the class can be affected by the specific chemical structure and also by the use of coinhibitors or blends.

The various inhibitors are reactive with either platinum catalyst or cross-linker and so dictate how the various components can be combined and how complex or simple customer-level formulating can be.

Next on the list of components is the cross-linker. As mentioned previously, the two general types are homopolymers and copolymers, but these can also range in molecular weight and degree of dimethyl substitution. Both will have an impact on cure rate, bath life, and anchorage. Additional formulating flexibility is provided by adjusting the ratio of cross-linker to polymer, usually referred to as the SiH to vinyl ratio (SiH:Vi) on a molar basis. Excess SiH is required to progress the cure at a reasonable rate. Ratios from 1.1:1 at the lowest level up to 2.5:1 at the highest level are used. Higher SiH:Vi ratios can be used to improve anchorage on some substrates. Lower SiH:Vi ratios are often employed when it is desirable to minimize the interaction with reactive adhesives.

As mentioned previously, it is sometimes necessary to alter the release force with the use of a release modifier. Although this will be discussed in more detail in the next section, it should be noted here that the addition of release modifier will also impact other aspects of performance, such as cure rate, coverage, and anchorage, sometimes positively and sometimes negatively. The effects are somewhat complicated and must be addressed on an individual case-by-case basis.

Other additives can be incorporated in a release coating to improve processing and performance, most specifically, mist reduction and anchorage. In high-speed processing of solventless coatings, fine and often visible mist is generated during the film splitting that occurs as the coating is passed from one process roll to the next. The use of antimist additives or mist-reducing agents will minimize this effect and allow processing of solventless silicone coatings up to at least 3,500 feet per minute (fpm) (ca. 1,000 m/min). The generation of mist and the effectiveness of the mist-reducing agents are affected by coating viscosity, polymer architecture, and various process variables such as coat weight, roll speeds and ratios, roll diameter, and rubber roll covering.

9.3 Controlling Release Force Profiles in Silicone Liner-Enabled Pressure-Sensitive Adhesive Constructions

The manufacture and use of pressure-sensitive products (PSPs) involves multiple steps or operations, each of which may impose a different set of requirements on the release coating (see Figure 9.15).

The basic operations include coating and curing the release coating (making the release liner); coating and curing, or laminating, the adhesive or tacky material, and subsequent laminating of a face stock or other protective substrate to the tacky surface; slitting, cutting, die-cutting, or shaping the pressure-sensitive laminate and then removing the excess (as in matrix removal of a label face stock) (see also Chapter 10); and delaminating and dispensing the pressure-sensitive material to its final destination (see also *Applications of Pressure-Sensitive Products,* Chapter 4). During production of the release liner, the release surface may be used immediately or rolled up and stored for later use (referred to as in-line versus off-line use). The state of cure of the release coating and the coverage of the substrate can have a great impact on release during all operations.

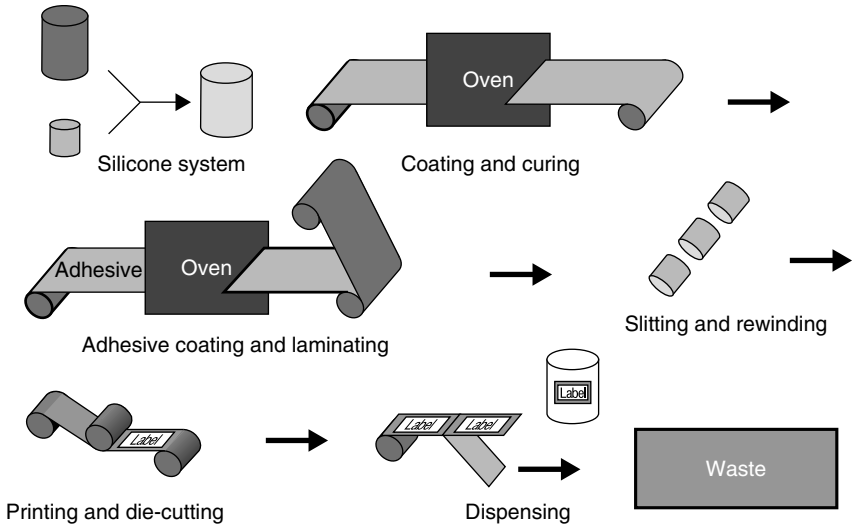


FIGURE 9.15 The life of a pressure-sensitive release coating.

For in-line lamination, it is preferable to progress the cure of the coating as much as possible prior to mating it with either wet or cured adhesive. This may require longer dwell times or higher cure temperatures and often different formulations than off-line operations. Although off-line operations have the luxury of allowing for some postcure of the silicone coating, merchant suppliers of release liners often go to great lengths to provide an inert, well-cured silicone surface for their customers. Silicone coverage of release liners from merchant coaters is often far superior to those produced by in-line laminators.

Release force can be measured at a range of peel or delamination speeds and in a variety of configurations, for example, liner from label versus label from liner, and peel angle (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Butt-cut and hand-peeled labels allow for a very wide range of release forces and are not very demanding. Die cutting and matrix removal, however, are done at somewhat moderate speeds (200–500 fpm), but can be done at a variety of peel angles, depending on the press setup (see also Chapter 10).

It should not be forgotten, however, that matrix removal imposes a greater speed and angle because the excess matrix travels horizontally across the web in addition to vertically downweb. In an attempt to utilize as much laminate surface as possible, matrices can be cut very thin, reducing their ability to withstand the force of removal. Most matrix breaks on printing presses occur in the horizontal direction as the matrix attempts to keep up with press speed.

Labels are dispensed anywhere from the grocery store hand-held method to high-speed labeling lines running in excess of 1,000 labels per minute (see also *Applications of Pressure-Sensitive Products*, Chapter 4). In all cases, however, the removal of the liner from the label is a start–stop operation, so removal begins at zero and progresses up to

full speed. This can be mimicked by a ramped peel on lab testing equipment. Important aspects of this operation are that there be minimal initiation of release (no initial hurdle to begin peel) and minimal zippiness or chatter. The former can lead to unlabeled containers or bottles and the latter can lead to matrix breaks during die cutting/stripping or to visible imperfections/lines in the label face. Equally disastrous is the release that is too easily initiated or propagated so that labels come off during die cutting/stripping, leaving gaps in a roll of labels, or so that labels predispense (Sections 9.1 through 9.3 are drawn from Jones [1]).

9.3.1 Why Silicones Are Effective Release Coatings

PDMS has several unique properties. The high flexibility of the siloxane backbone (Si–O–Si bond angles from 140 to 180) and small barrier to linearization (0.3 kcal/mol) [2,3] (Table 9.3) allow the dimethyl groups to populate the air interface. The resulting surface tension for typical PDMS systems used for release coatings is 21 to 22 mNm^{-1} [4]. This is significantly lower than the surface tension of typical organic pressure-sensitive adhesives (PSAs), which have surface tension values of roughly 30–50 mNm^{-1} [5]. Consequently, when an organic PSA is applied to a silicone release coating it lacks the thermodynamic driving force necessary for complete wetting of the silicone coating. Hence, it avoids intimate contact (an initial requirement for adhesion) with the silicone coating, which assists with the eventual release of the PSA.

Low surface energy alone, however, does not guarantee a good release surface. The extreme flexibility of the silicone backbone enables the PDMS molecules to move freely over a wide range of temperatures and frequencies, as evidenced by the extremely low glass transition temperature (T_g) for PDMS of −120°C [4]. Also, PDMS is a semicrystalline polymer with a melting temperature (T_m) near −45°C, but at normal use temperatures the PDMS chains are amorphous. When the PDMS polymer chains are cross-linked into a silicone coating, the free mobility of the polymer segments between the cross-link sites makes the resulting silicone coating very elastic. Elastic materials efficiently store energy and return it when the energy source is removed. Consequently, when a PSA is peeled from the silicone release coating, the peeling energy that is transferred to the silicone release coating is stored and concentrated at the PSA/silicone interface, making it readily available for propagating the interfacial crack, which leads to low release forces [6].

TABLE 9.3 Properties of Siloxanes versus Carbon Equivalents

Properties	Silicon		Carbon	
Bond energies	Si–O	445 kJ/mol	C–O	358 kJ/mol
	Si–C	306 kJ/mol	C–C	346 kJ/mol
Rotational energies	Si–O–Si	~0 kJ/mol	C–C	14 kJ/mol
Bond angles	–Si–O–Si	145°	–C–O–C	111°
Bond lengths	–Si–O	0.163 nm	–C–O	0.142 nm

Note: Siloxanes have highly flexible backbones, large bond angles, long bond lengths, and extreme freedom of rotation compared with organic polymers.

In summary, the low surface tension of PDMS prevents the PSA from fully wetting the release coating, and the coating's elastic character minimizes the energy necessary to separate the imperfect interface between the two materials. Low release forces result, making silicone coatings the material of choice for releasing many PSA systems. If every PSA release application required minimized release forces, it would be possible to have a one-coating-fits-all solution. However, because low, but not always the lowest, release forces are desired for a given system and application, it has been necessary for silicone release coating producers to develop methods to tune release forces and release force profiles into their coatings. In the sections that follow, approaches to tune release forces will be discussed, followed by methods to tune the release force profile (release force versus peel rate), which involves consideration of the PSA material properties as well.

9.3.2 Approaches to Control Release Forces from Silicone Release Coatings

Controlling release force properties, and doing so in an accurate and consistent way, remains arguably the most difficult technical challenge in silicone release coating technology. The two main approaches that have been used by release coating manufacturers for tuning release forces are through controlling the cross-link density of the coating and the addition of a silicate resin-based high-release additive (HRA).

9.3.2.1 Cross-Link Density Control

Historically, silicone release coatings have been delivered to the substrate using a solvent to tune and optimize the coating viscosity for a given coating process. The neat viscosity of the polymer chains and hence their viscosity were not a concern because the solvent content could be adjusted to achieve the viscosity necessary for efficient and effective processing. Tin-catalyzed condensation-cure silicone coatings were the workhorse solvent-delivered silicone coating system at one time. These products are still used today but only in select applications, primarily due to the desire and regulatory activity to remove unwanted tin and solvent components [7].

9.3.2.1.1 Cross-Link Density Control in Solvent-Delivered Systems

In tin-catalyzed solvent systems, the molecular weight of the PDMS chains used in forming the cured polymer network was the primary tool used to control release forces. Figure 9.16 illustrates how the release forces could be increased in these systems efficiently and controllably by varying the degree of polymerization of the silanol-terminal PDMS component of the release coating from 20 to 5,000 units. In these systems, the primary PDMS coating characteristics responsible for release, namely low surface tension and very elastic behavior, remain intact.

However, the cross-link density of the silicone coating and, consequently, its modulus and ease of elongation are altered. In practical terms, the highest molecular weight polymers give soft coatings with very high elongation. The 600-unit polymers give fairly hard coatings with approximately 20% elongation at break. Comparatively, the very short-chain polymers yield cross-linked coatings that are quite brittle and inflexible, and so elongation at break is often too low to measure.

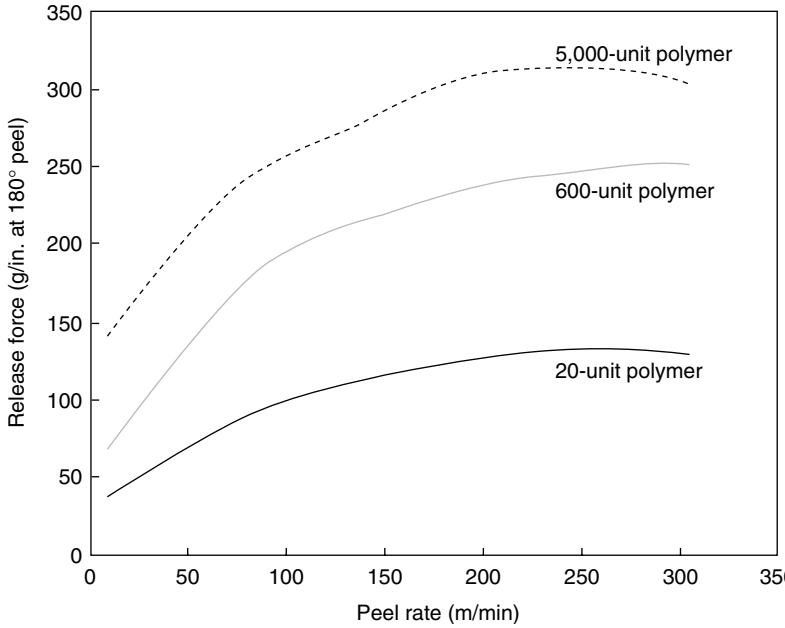


FIGURE 9.16 Impact of polymer molecular weight on the release force of a PSA from solvent-delivered tin-catalyzed silicone release coatings.

During release, the PSA is pulled from the release coating. As the PSA/release coating interface separates, both components undergo elongation until a critical interfacial stress is exceeded, at which time the materials separate. The energy associated with the elongation of both components contributes to the measured release force. By increasing the PDMS chain length, the cross-link density and modulus are decreased and elongation of the silicone release coating is increased. The lower modulus of the silicone coating enables both the coating and the PSA to elongate further before the critical interfacial stress is surpassed, requiring more energy for the peel event and higher release forces.

A secondary effect of reducing the modulus of the release coating can be enhanced contact between the silicone and the organic PSA. The lower-surface-tension silicone component possesses a thermodynamic driving force to wet the higher-energy PSA, minimizing interfacial tension; but its mobility is restricted to the motion of the chain segments between cross-links [6]. By increasing the molecular weight of the PDMS component, the resulting increase in mobility of PDMS segments between cross-links enables more complete wetting of the PSA, increasing the integrity of the interface and the release force required for failure.

9.3.2.1.2 Cross-Link Density Control in Solventless Systems

Environmental pressures have created a trend toward solventless release coating systems such that addition-cured solventless systems are now the preferred technology in the industry.

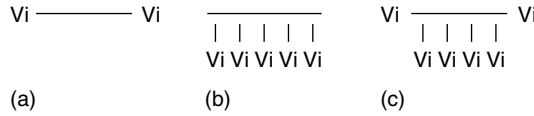


FIGURE 9.17 Polymer structures used in solventless release systems.

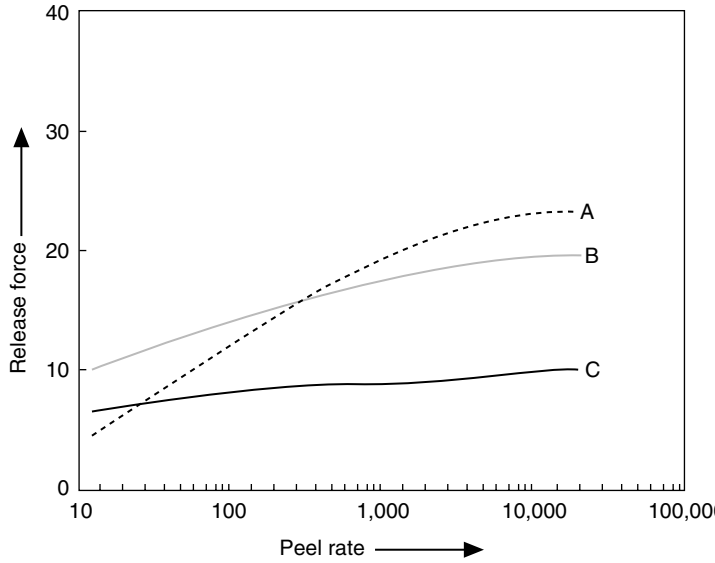


FIGURE 9.18 Impact of polymer structure on release profile.

The building blocks for this system are polymers with only terminal reactive groups, only side-chain reactive groups, or both. For a solventless system to be coatable on the roll coaters typically used for application, it is desirable that the polymers should be no longer than approximately 300 siloxane units, preferably in the 100- to 200-unit chain length range (see Figure 9.17).

During processing and following cross-linking, these shorter-chain-length polymers have significantly less extensibility available than the long, high-viscosity polymers. The release behavior of the solventless systems based on the three types (A, B, and C) of vinyl functional polymers are illustrated in Figure 9.18. Within these types, however, molecular weight, especially with terminal-only polymers (A), can be used to adjust the specific release forces and flatten the release profile to some extent. As the terminal-only polymers become short enough to provide high cross-link density coatings, however, the viscosity becomes too low to allow coating on typical roll coating equipment. Increasing pendant functionality on either the multifunctional or pendant-only polymers can further flatten the release profile; but at some point, this only adds cost and no longer contributes to release profile adjustment and can negatively affect adhesive compatibility or release stability.

Figure 9.19 illustrates that the range of release forces achievable with the solventless addition cure system is greatly reduced compared to the solvent-delivered condensation system.

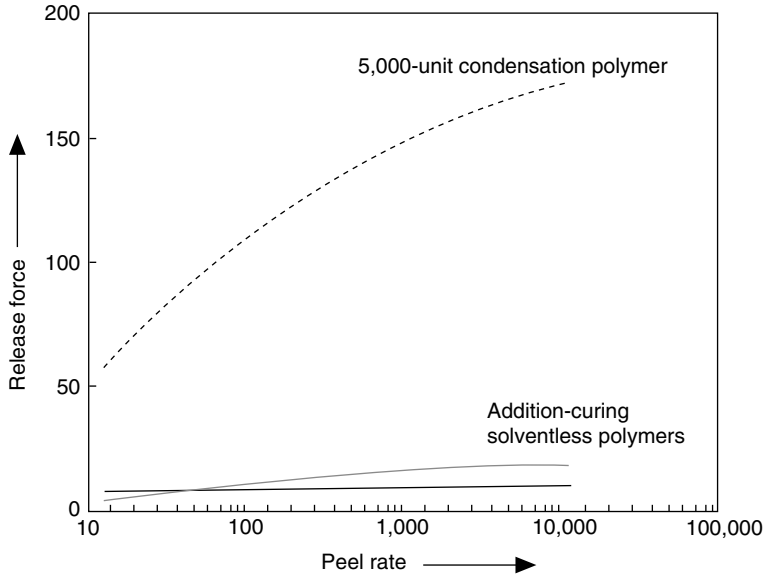


FIGURE 9.19 Comparison of relative release force profiles of condensation-cured solvent-based and addition-cured solventless polymer release coatings.

To close this gap, silicate resins are commonly added to the solventless systems to increase the release forces to values appropriate for the wide range of potential applications. The role of silicate resins in controlling release forces from silicone coatings will be discussed in detail in the following sections.

9.3.2.2 Addition of Silicate Resin High-Release Additives into the Silicone Coating

Silicate resins increase the release forces from silicone coatings primarily by increasing the dissipative character of these otherwise very elastic (nondissipative) materials. The surface tension of the silicate resins is almost identical to that of PDMS, so that addition of the resins has negligible impact on the surface tension of the system. Silicate resins were first used with the solvent-based release coatings as an additional tool to controllably raise release forces beyond what could readily be achieved by raising PDMS molecular weight (discussed in Section 9.4). However, as environmental pressure against solvent emissions and tin catalysts has grown, the industry has moved to primarily 100% solids or solventless systems that are addition cured and now utilize silicate resins as the primary tool to controllably enhance release forces.

Silicate resins, or *MQ* resins (*M* is a monofunctional siloxy group with three organic constituents and *Q* is a tetrafunctional siloxy building block with no organic groups), are rigid silicone materials with an effective glass transition temperature (T_g) (or softening temperature) above 200°C for *M*:*Q* ratios of $<$0.8. Figure 9.20 illustrates a molecular model of an average structure for an *M*0.8*Q* resin. The primary structural unit is a

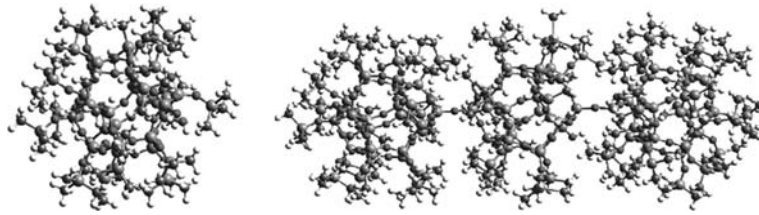


FIGURE 9.20 Molecular models of *MQ* silicate resin cage and linked cage structures.

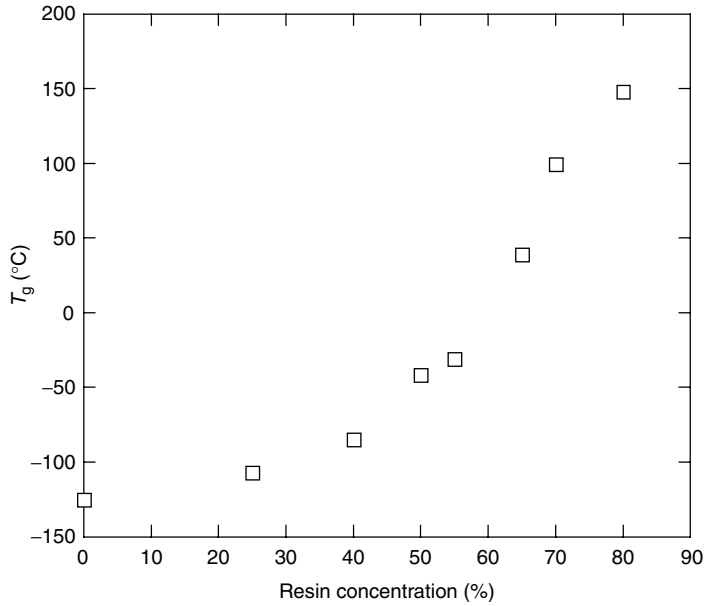


FIGURE 9.21 Impact of *MQ* resin loading on the glass transition temperature (T_g) (temperature of major maximum in tan δ) of *MQ*/PDMS blends.

cage of *Q* units surrounded by a methyl-containing *M*-unit shell; once the molecular weight of a single cage structure is exceeded, additional molecular weight growth occurs through linking cages. Consequently, as molecular weight growth occurs in *MQ* resins, initially, branched structures are formed until the molecular weight is large enough for the structure to collapse into cyclic structures. As the cyclic structures grow, eventually they collapse into three-dimensional cage structures, which in turn grow in molecular weight via interlinked cages.

Because of their methyl siloxane shell and small size (1–3 nm), these *MQ* materials are compatible with the low-T_g PDMS polymer (T_g −120°C) over the entire blend composition range and are uniquely capable of dramatically increasing the effective glass transition temperature of the blend, dependent upon the level of *MQ* loading, as depicted in Figure 9.21.

Cross-linked polymers exhibit very elastic (rubbery) behavior at temperatures exceeding the T_g by >70°C [8]. However, polymeric materials exhibit much more energy-dissipative

behavior in the vicinity of the glass transition regime, so that using the *MQ* resins to move and position the T_g of the silicone release coating nearer to use temperatures adds some dissipative character to the otherwise elastic PDMS network. By increasing the dissipative character of the silicone release coating in a controlled manner, the release forces of an adhesive construction can likewise be increased controllably.

The use of *MQ* resins as HRAs through positioning the T_g of silicone release coatings in the vicinity of room temperature provides an efficient manner to increase the dissipative character of the silicone coating while still maintaining low surface tension. But, as the name suggests, the glass transition is a region of temperature and frequency where the material undergoes a large transition from an elastic rubber to an elastic glass. In the transition region between these two extremes is a region of viscoelastic behavior that is very temperature and rate dependent and where the loss character of the material becomes significant so that the material becomes effective at both storing and dissipating energy. As a result, achieving high release forces with resin HRAs usually brings with it considerable release force dependence upon the speed (frequency) and temperature of the release event [6].

MQ resin HRAs are typically introduced into the release coating system at loadings of 15–80 wt % based on the solids content of the coating formulation and the resin content of the HRA. As illustrated in Figure 9.21, it is not until the resin content approaches 40 wt % that the system glass transition temperature increases appreciably. However, from 45 to 60 wt % loading, the blend T_g increases dramatically (>60°C), and the release forces increase significantly as well.

9.3.2.2.1 Silicate Resin Options (Functional and Nonfunctional Resins)

In addition-cured systems, the resin HRA is traditionally designed to chemically tie into the polymer network via vinyl groups on the resin, respectively. By chemically bonding to the coating network, the resin is rendered nonextractable, which is a requirement of many adhesive system converters to avoid the possibility of silicone components migrating to the PSA surface and interfering with subsequent adhesion in the target application. A consequence of chemically bonding the resin to the polymer network is an increase in the cross-link density and, hence, storage modulus of the coating with increased HRA loading. In Section 9.3.2, it was revealed that an increase in cross-link density reduces release forces, which is counter to the purpose of an HRA. Consequently, some of the increase in release forces resulting from the enhanced dissipative character the HRA provides is sacrificed by the increase in cross-link density that occurs when chemically tying the resin into the network.

To obtain maximum efficiency from a silicate resin HRA, it is possible to avoid tying the silicate resin into the polymer network and thereby avoid an increase in the cross-link density of the coating. In fact, if nonfunctional *MQ* resins are used as an HRA, the storage modulus of the silicone coating actually decreases slightly owing to the lubricating effect of the resin [9,10]. The silicate resins are particulate in form and, consequently, lack the ability to reptate through the coating like an untethered polymer chain. As a result, a nonchemically bound silicate resin should not be able to migrate to the PSA surface and interfere with subsequent adhesion of the PSA following release.

However, a loose silicate resin particle will be readily extracted from the silicone coating by a good solvent so that use of nonfunctional resins will lead to an increase in

extractable content, which could be unacceptable for select applications. Migration of a particle and extraction of a particle with a good solvent are controlled by different physical phenomena, which make it possible to have extraction without migration. If a good solvent for the resin particle is avoided during construction of the PSA/release coating system, a nonfunctional resin should be considered to obtain maximum efficiency for increasing release forces (increase dissipative character and decrease modulus).

Figure 9.22 illustrates the impact of *MQ* HRA loading on the dynamic mechanical properties of a cured silicone release coating at 25°C over a broad range of frequencies [6]. In this work, the HRA contained a 50/50 by weight blend of vinyl-functional silicate resin and vinyl-terminal polymer. It is apparent that the addition of the HRA enhances the loss modulus, G'', of the release coating to a greater extent (from 3×10^4 to over 6×10^5 Pa at 10^5 rad/s) than that of the storage modulus G' (increase is significantly less than an order of magnitude). The increase in the loss modulus is directly related to the increase in the dissipative (or loss) character of the release coating. Figure 9.22 also illustrates the frequency range of interest for typical release processes and a silicone film thickness of 1.5 μm. At high HRA loadings (80 wt % HRA, 40 wt % silicate resin), the storage modulus (G') of the release coatings starts to turn upward with enhanced frequency, signaling the start of the glass transition regime where the loss character of the material becomes more significant.

Figure 9.23 illustrates the release force profiles for an industry standard acrylic (*tesa*® 7475) and rubber-based (*tesa* 7476) adhesive from the HRA-modified silicone release coatings [6]. Addition of the HRA increases release forces steadily at any given peel rate

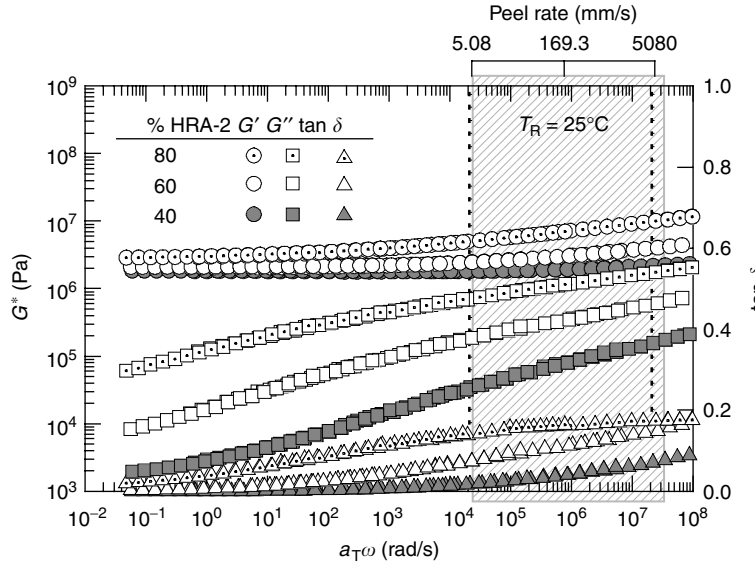


FIGURE 9.22 Rheologic master curves (25°C) for the release coating material at three HRA-2 concentrations. The dotted lines bracket a 3-decade frequency window corresponding to the range of rates used in peel testing based on a nominal coating thickness of 1.5 μm. (From Gordon, G.V. and Schmidt, R.G., *J Adhesion*, 72, 133, 2000. With permission.)

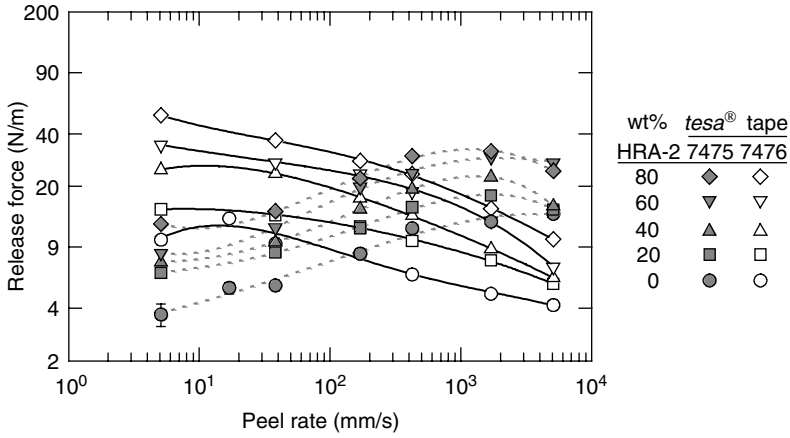


FIGURE 9.23 Logarithmic plot of release force as a function of peel rate for a silicone-coated liner (modified with 0–80 wt % HRA-2) peeled at a 180° angle from two different PSA tapes: *tesa* 7475 with an acrylic-based adhesive and PVC backing, and *tesa* 7476 with a rubber-based adhesive and cloth backing. (From Gordon, G.V. and Schmidt, R.G., *J Adhesion*, 72, 133, 2000. With permission.)

for both adhesives, demonstrating the ability of silicate resin HRAs to enable a specific release force to be tuned within select ranges for select PSA systems. However, it is apparent from Figure 9.23 that the trend of the release force profile clearly can vary, depending on the adhesive used, with the acrylic PSA release force increasing with peel rate while the rubber-based PSA exhibits the opposite trend. In Section 9.3.3, strategies for achieving control of the release force profile shape will be discussed.

9.3.3 Controlling the Shape of Release Profiles

Controlling the shape of release force profiles can be very important in applications such as applying adhesive labels to product containers at high speeds. An inappropriate release profile can lead to labels missing their intended location due to premature or delayed release. When considering control of the release profile, it is the total construction that is under consideration. In the case of a typical PSA label construction, the silicone release coating is about 1/15 to 1/20 the mass and thickness of the adhesive; therefore, the energy management of the PSA during release has a very large and potentially dominant impact on the release force and profile.

In 2000, Gordon and Schmidt [6], inspired by pre-existing adhesion models, proposed an empirical release model based on the viscoelastic properties of the adhesive and release coating to describe release force profiles. In this work, the release force of an acrylic- and rubber-based PSA from silicone release coatings containing different levels of HRAs was measured as a function of peel rate. The release profiles differed dramatically for the two different adhesive types (Figure 9.23). The general trends of either increasing or decreasing release force profiles with peel rate were proposed to be predominantly due to the adhesives' relative ability to dissipate and store energy (tan δ) over the operating

frequency range. The authors concluded that the adhesive type and thickness must be chosen properly, along with an appropriate HRA concentration to achieve the desired release force level and profile.

9.3.3.1 Viscoelastic Properties of Pressure-Sensitive Adhesives

Although the viscoelastic properties of PSAs are addressed in detail within other contributions to this work (see also *Fundamentals of Pressure Sensitivity*, Chapters 1, 4, and 5), a brief discussion is included here to illustrate their role relative to the release profile. High-performance PSAs, which are typically utilized in a cured state, must have the ability to efficiently form physical bonds with substrates under relatively low-frequency conditions and resist debonding under considerably higher-frequency peel conditions. To accomplish both tasks with one material, a low modulus is required under bonding conditions [11], and a significantly higher modulus with a large dissipative component is required under higher-rate debonding conditions [12,13]. Consequently, PSAs typically have very dynamic moduli profiles near standard-use temperatures and frequencies.

Figures 9.24 and 9.25 illustrate the shear storage (G'), loss (G'') modulus, and the loss tangent ($\tan\delta = G''/G'$) master curves for the acrylic- and rubber-based adhesive materials (unsupported) used in the study by Gordon and Schmidt [6].

Based on the measured thickness of each adhesive, the resulting frequency window corresponding to the delamination rates used in the study (5–5,000 mm/s at 25°C) for the acrylic ($h = 82$ μm) and rubber ($h = 40$ μm) adhesive are depicted by the dotted vertical lines in Figures 9.24 and 9.25, respectively (estimated using $\nu = \frac{\omega}{2\pi}h$, which relates

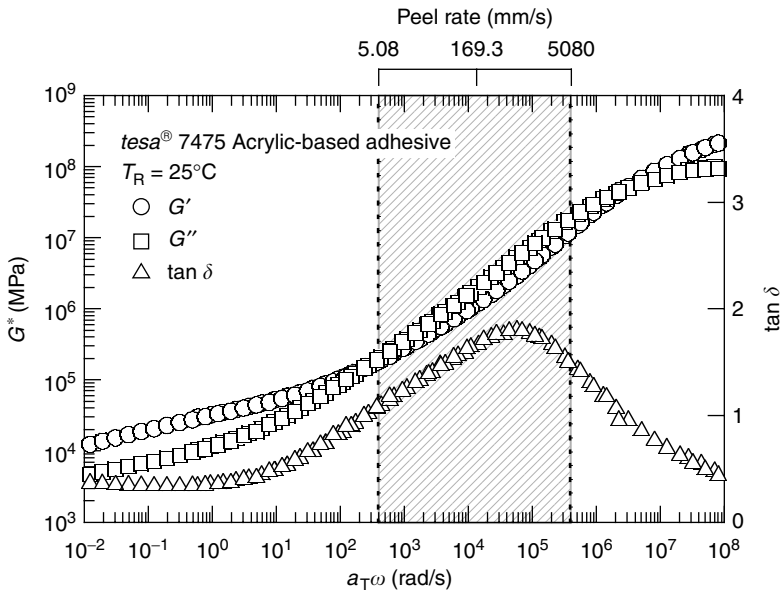


FIGURE 9.24 Rheologic master curves (25°C) for *tesa* 7475 acrylic-based PSA. (From Gordon, G.V. and Schmidt, R.G., *J. Adhesion*, 72, 133, 2000. With permission.)

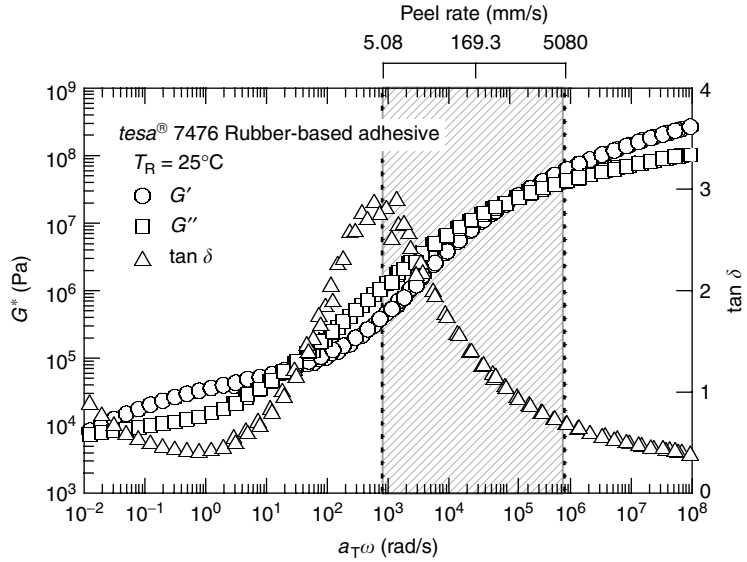


FIGURE 9.25 Rheologic master curves (25°C) for *tesa* 7476 rubber-based PSA. (From Gordon, G.V. and Schmidt, R.G., *J Adhesion*, 72, 133, 2000. With permission.)

the effective dynamic frequency (ω) of deformation subjected on each of the system components to the rate of delamination (υ) by accounting for the thickness (*h*) of a given component in the peel test [14]. It is apparent that over the applicable frequency range of the release event, the storage and loss characteristics of the PSA change dramatically. Most notably, the change in the loss tangent of the PSA over the applicable frequency range has been proposed as having a direct impact on the shape of the release profile. Consequently, one can alter the release profile most dramatically by changing the adhesive composition and, to a lesser extent, by changing the effective frequency range by changing the adhesive thickness. In both cases, a high-release additive can then be added to the silicone coating to further manipulate the magnitude of the release forces while typically maintaining the same trends in the profile as dictated by the PSA.

9.4 Choosing a Silicone Release Coating

9.4.1 Market/Applications

The biggest single use for release coatings is to make release liners that carry and protect PSAs until the moment of use. For this application, the most important substrate is paper. PSA-coated materials include labels, tapes, overlaminating films, sign lettering, medical devices, and a host of smaller applications. Other markets for release liners that are non-pressure-sensitive applications include carriers for oily and sticky masses

such as sealants, gaskets, mastics, tiles, and shingles; interleaving layers for rubber processing; and support and release base for the casting of plastic films such as polyethylene (PE), polyurethane (PUR), acetate, and vinyl films. Liners in the final group are often embossed to impart texture to the cast film. Further examples of release liners include food-processing aids such as baking or pan liners; food-packaging materials such as gum wrappers; asphalt packaging, in the form of coated drum interiors; release-coated inner layers of paper sacks; and caul or separating sheets for the production of high-pressure plastic laminates.

The end uses of these PSA constructions are as varied as the constructions themselves. PSA products are used in the medical, construction, automotive, graphic arts, electrical, and electronic industries. Electronic data processing consumes vast quantities of pressure-sensitive labels, most of which turn up in the average household as address labels on bills and advertising material. Supermarkets also use significant quantities of pressure-sensitive labels as price-weigh labels, special-offer labels, and in the form of a complex label that also includes a discount coupon (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Most of today's special mail and package delivery operations use pressure-sensitive bar code labels as check systems to monitor the progress and delivery of packages. Radiofrequency identification labels and systems are projected to eventually replace those used today (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Labeling systems are being developed to provide hospitals with permanent records of patient treatment and progress (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Most of today's tamper-resistant packaging and security labels are based on some form of pressure-sensitive labeling system (see also *Applications of Pressure-Sensitive Products*, Chapter 4). The list is endless and grows daily as greater and greater innovation is displayed by the pressure-sensitive industry.

As pressure-sensitive systems displace mechanical forms of fastening, so too are there alternatives to pressure-sensitive labels in packaging identification. The major benefits of pressure-sensitive over alternative labeling systems are cost and flexibility, allowing rapid changes in design and style.

In the tape field, the most familiar types, such as masking and office tape, do not normally involve the use of silicone release materials (see also *Applications of Pressure-Sensitive Products*, Chapter 4). However, tapes have a very wide range of capabilities and uses, some of which are very sophisticated and specialized in the industrial world. Electrical insulating, wrapping, thermal insulating, decorating, and especially bonding tapes are all areas in which silicone release coatings find use. Specialized markets for release coatings and liners have developed in the industrial and medical fields. In the manufacture of carbon-fiber/epoxy laminates, such as those used to produce aerospace craft and sporting goods, silicone release liners provide a release range and stability not found with other materials because the materials go through a wide range of storage temperature and processing conditions. Medical devices and treatments in the form of diagnostic equipment and wound dressings can be quite complex and use aggressive, reactive materials that must be protected during manufacture, storage, and even in use. Various silicone release materials and substrates are used to serve these markets (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

9.5 Current Trends Influencing Technology Development

Of all the market trends affecting pressure-sensitive release applications, the most overriding is cost reduction. Indeed, most of the advances in technology, whether equipment or materials, can be attributed to some desire to ultimately reduce cost. Most directly related to cost reduction are the following.

- Increased coating line speed—requires faster-curing silicone materials
- Energy-savings/low-temperature curing—requires lower-temperature-curing silicone materials
- Increased converting and dispensing speed—requires redesign of silicone architectures to provide desired release profiles
- Substrate selection and down-gauging—requires silicone coatings that provide easier release
- Lower cost-in-use—requires silicone coatings that spread/wet substrates faster or allow lower silicone coat weights

Let us be more specific on the demands these trends have placed on silicone release materials and the responses by silicone manufacturers. Line speeds for coating silicone release coatings have increased from 1,500 fpm in the early 2000s to 3,500 fpm today. To be fair, production equipment design has allowed dwell times to remain the same by incorporating longer-curing ovens. The faster line speeds, however, have led to more demand for mist-reducing agents and for lower-viscosity silicone materials that can be transferred via roll coating equipment to the web and then spread and wet on the substrate prior to gelation.

Energy costs have inflicted themselves in a number of ways. The rising cost of energy has refueled the desire to accomplish silicone cure at lower temperatures. If the substrate is paper, this allows for a lower level of moisture removal from the paper, thus requiring less energy for remoisturization. Rising costs for transportation have led to a desire to increase the yield of labels per square footage, resulting in down-gauging of both liner and facestock, and in label design to yield a smaller area of matrix removed. At the same time, increases in converting (die-cutting/matrix stripping) speeds have put more strain on the matrix/face stock, and increases in dispensing speeds have put more strain on the liner. Overall, smoother, stronger liner substrates are needed to keep up with these trends.

The predominant substrate for pressure-sensitive label production is densified kraft, more specifically, supercalendered kraft in North America and glassine in Europe and other parts of the world. Clay-coated kraft papers are often used for their lay-flat characteristics and dimensional stability in such applications as graphic arts. The clay/latex coating must be formulated to avoid ingredients that will inhibit platinum. Many very good clay-coated papers are available for siliconizing, but others have severe cure or anchorage issues. Improvements in densified paper liners have included attention to smoothness, caliper control, better yield, and improved silicone holdout, along with a general trend in down-gauging.

Although smoother paper with better holdout allows lower silicone coat weight, the surface treatments that have been used to achieve this often affect silicone anchorage. This begins a whole matrix of requirements and adjustments in the silicone, including polymer and cross-linker selection (remember that cross-linkers that provide better anchorage are not always optimum for fast cure), and can affect catalyst requirements. Down-gauging to lower-basis-weight paper changes the actual angle of peel, which creates higher release and ultimately requires silicones that provide lower release and less use of release modifiers. A natural shift to filmic substrates as release liners for smoothness and strength/weight ratio has occurred, but the improvements in converting operations are not provided without increased cost in materials.

Polyester, oriented polypropylene, and polyethylene are increasingly used in all areas, whereas polyolefin-coated kraft papers have a large share in Asia. The polyolefin family is wrought with substances such as antioxidants and other process aids that wreak havoc with silicone cure. The added limitation of lower temperature resistance makes silicone cure quite difficult. In addition, polymer and cross-linker selections are more limited. Polyester has a higher tolerance for temperature, so it is easier to push up in dwell time at temperature to accomplish cure; however, anchorage is notoriously difficult to achieve and maintain. New silicone polymer architectures and anchorage additives for thermal-cured systems have addressed this to some extent, but more collaboration between film/resin suppliers and silicone suppliers to make films more silicone-friendly would certainly help extend their range of utility.

Many times the adhesive or sticky material that is mated to the silicone release coating is reactive or may have ingredients that attack the silicone coating. These can result in phenomena such as unstable release, no release, and loss of anchorage. The most familiar phenomenon is referred to as "acrylic lock-up." This results from residual SiH in the silicone reacting with acrylic acid in an acrylic adhesive, being catalyzed by the platinum catalyst in the silicone.

Not all acrylic adhesives have this issue. It is particularly prevalent with solvent-based acrylics because they are more frequently formulated with excess acrylic acid, and self-cross-linking formulations contain additional catalytic species. Tin-catalyzed silicone release coatings avoid this through absence of the catalyst that promotes the reaction. Rhodium-catalyzed silicone release coatings avoid this by nature of the rhodium catalyst not being particularly active at room temperature or temperatures used to cure the adhesive. Platinum-catalyzed release coatings can be formulated to minimize this phenomenon by using a lower SiH:Vi ratio, lower vinyl content polymer, hexenyl versus vinyl polymer, and curing to completion prior to adhesive casting. Some hot-melt adhesives have demonstrated phenomena similar to acrylic lock-up, and similar alterations in silicone will abate the problem.

Water-based acrylics rarely yield this phenomenon, but can result in other issues. In particular, the most commonly observed issue is that affecting anchorage. A silicone-coated liner can exhibit excellent anchorage; but after adhesive coating and storage of the laminate, eventually the silicone coating will exhibit rub-off, or loss of anchorage. This phenomenon is attributed to migration of ingredients from the adhesive coating package, such as surfactants, to the silicone or silicone/substrate interface, and degrading the integrity of the silicone coating. Sometimes attention to silicone coating,

through ensuring excellent coverage and even applying excess silicone coat weight, can help alleviate this issue, but not always. Additional platinum catalyst, a higher SiH:Vi ratio, homopolymer cross-linker, and anchorage additives can also be used, assuming reformulation of the adhesive is not a possible or desired option.

Nonadhesive materials such as the tacky mastics or roofing asphalt can have oily materials in them that migrate to the silicone/adherend interface and alter release characteristics. Again, special formulating and silicone selection can help alleviate this situation.

9.6 Summary

The information provided in this chapter is meant to inform those using silicone release coatings or silicone-coated release liners of the various options available and how they impact the many aspects of producing PSPs. It is not intended to make the reader self-sufficient in selecting and formulating silicone release coatings. It should be obvious after reading this chapter that in some cases the optimum formulation can be selected to meet all the requirements for processing, cure, compatibility, and release, but in other cases compromises will need to be made that require prioritization of performance needs and possibly changes to formulations or process conditions that would otherwise not be preferred. The range of formulated materials and intermediates is such that, in most cases, a solution can be identified.

The surface properties of silicone release liners for PSAs are clearly important for enabling the development of a release system. The low surface energy of silicone release coatings, which limits the work of adhesion and molecular entanglement that can develop at the interface between the silicone coating and organic PSA, provides the basis for the widespread use of silicones as release coating materials. The primary methods used to control release forces over finite ranges are either by manipulating the elongation of the release coating system by controlling the chemical cross-link density or by increasing the dissipative character of the release coating through the use of silicate resins. These approaches provide convenient control of release forces at any given delamination rate. However, to control the shape of the release profile, the viscoelastic properties of the PSA over the relevant rates must also be considered. Owing to the large mass of the PSA relative to the release coating, the energy management of the PSA during release has a very large and potentially dominant impact on the shape of the release profile.

Silicone release coatings still dominate as the material of choice for PSPs, whereas nonsilicone materials are available for performance outside the range of capability of silicones. Suppliers of silicones continue to invest in the mechanistic understanding of cure and release and try to keep up with the changing world of PSPs as well as other labeling and identification methods, and, in the case of tapes, fastening and bonding techniques. As new adhesives, substrates, and processing equipment are developed, the need to adjust existing or develop new performance from silicones continues to be a challenge. So far, no materials have exhibited the breadth of capability of silicones for this demanding set of applications.

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10

Manufacture of Pressure-Sensitive Products

10.1 Manufacture of Pressure-Sensitive Adhesives **10**-2
- Manufacture of Solvent-Based Adhesives
- Manufacture of Water-Based Adhesives
- Manufacture of Hot-Melt Adhesives

10.2 Manufacture of Pressure-Sensitive Products **10**-9
- Manufacture of Other Web-Like Components
- Web Finishing

10.3 Conversion of Pressure-Sensitive Products **10**-41
- Confectioning • Other Conversion Methods

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Pressure-sensitive products (PSPs) are multilayer constructions based on solid-state materials and coated components (see *Applications of Pressure-Sensitive Products*, Chapter 1). Therefore, the production of the PSPs includes the manufacture and assembly of the individual components. The manufacture of the components includes the manufacture of both the solid-state carrier materials (face stock and release liner) and the coating components (adhesive, abhesive, primer, etc.) (see also Chapter 8). Generally, the build-up of the PSP from its components is carried out by coating and laminating and leads to a web-like product that must be confectioned. Table 10.1 presents the manufacturing technology of main PSPs and demonstrates that the manufacture of PSPs by coating of a solid-state carrier with a liquid pressure-sensitive adhesive (PSA) is the main procedure to produce various PSPs.

The principal coating component is the PSA. Other coating components are used to allow the anchorage of the adhesive on the carrier (e.g., primer; see Chapter 8) and its de-bonding from the laminate (e.g., release agent; see Chapter 11) and to protect or finish the adhesive or the carrier (e.g., printing inks, lacquers; see Section 10.2.4). Additives

TABLE 10.1 Manufacturing Possibilities of Self-Adhesive Products

Manufacturing Procedure	Parameter: Free Choice of Product Components		Parameter: Running Speed			Parameter: On-Line Manufacture	PSP
	Carrier	Adhesive	Very Good	Good	Fair		
Coating	•	•	•			•○	Label, tape, protection film
Extrusion coating	—	—		•		•○	Tape, protection film
Coextrusion	—	—			•	••	Tape, protection film

Note: ••, preferred; •○, possible.

that improve some special performance (e.g., electrical conductivity, flame resistance, recycling characteristics; see Chapter 8) can be coated on or built into the carrier material. The manufacture of solid-state components of PSPs was described in detail by Benedek in a previous book [1]. This chapter discusses the manufacture of the PSA and of the PSA-coated web, its conversion to a web-like laminate, and conversion of PSPs. Generally, the manufacture of adhesives includes their design [2], production [1,3], and quality assurance [4]. The test methods for quality assurance in adhesive manufacturing are described in *Applications of Pressure-Sensitive Products*, Chapter 8.

10.1 Manufacture of Pressure-Sensitive Adhesives

In the current practice, PSA manufacture is the formulation of adhesive raw materials synthesized off-line. Formulation influences the manufacture of PSPs and the global product technology, that is, manufacture and application, and determines the choice of the adhesive manufacturing and processing technology [4]. Off-line synthesis was discussed in Chapter 1; the role and methods of formulation were described in Chapter 8. As noted in this chapter, the formulation technology of PSAs is generally based on mixing various components of the adhesive, such as polymers and low-molecular-weight materials in a solid, molten, solved, or dispersed state. Such manufacture by mixing can differ according to the physical state of the adhesive; that is, dispersed adhesives or 100% solids-based PSAs need very different mixing technology.

Manufacture technology includes both the procedure and the equipment used to produce the adhesive. For PSAs with different physical states (i.e., water-based, solvent-based, or hot-melt adhesives) various elastomer- or viscoelastomer-based raw materials can be used (see Chapters 2 through 9 and 11). They also affect the formulating and coating technology and equipment. Certain raw materials are solid and others are liquid or must be transformed into a liquid system. Some raw materials must be mixed; other compounds are supplied in a ready-to-use form. Certain raw materials are supplied in a micronized state, whereas others are predispersed. Therefore, formulating equipment varies concerning the chemical basis of the adhesive (see also Chapters 1 through 8), the coating technology (see Section 10.2.2.1), and the PSP classes (see also *Applications of Pressure-Sensitive Products*, Chapter 1). The manufacture technology for PSAs used

for the main PSPs (labels, tapes, and protective films) was discussed separately for each product class by Benedek [1]. Ref. [1] covered the manufacture of various (common and special) PSPs as a whole, including both the solid-state components (e.g., face stock and release) and the liquid components (e.g., adhesive, release, primer). Our treatise is focused on the pressure-sensitive component of PSPs, that is, on the adhesive only. In the following sections the manufacture of PSAs according to their physical status (e.g., solvent based, water based, and 100% solids) will be briefly described.

10.1.1 Manufacture of Solvent-Based Adhesives

Solvent-based PSAs are tackified elastomers, tackified or untackified viscoleastomers, or tackified plastomers. Both (the tackified and the untackified recipe) need adhesive solutions as a blending medium; that is, mixing of the components occurs in solvents. Solvent-based adhesives were discussed by Benedek in Refs [1,4–7].

Classic, solvent-based adhesives were formulated with natural rubber (NR) and tackifier resins. Later, synthetic rubber-like products were introduced. Acrylics, vinyl acetate (VAc) copolymers, silicones, polyurethanes (PURs), and other viscoelastomers enlarged the choice of raw materials for solvent-based PSAs (see Chapters 1 through 11) and the diversity of the required equipment. Solvent-based acrylics need a special design, but less formulation, with the exception of special cross-linked systems [4]. The manufacture of solvent-based adhesives includes the technology (see Section 10.1.1.1) and the equipment (see Section 10.1.1.2).

10.1.1.1 Manufacturing Technology of Solvent-Based Adhesives

The manufacturing technology of solvent-based adhesives covers their formulation technology and the recycling of the liquid product components. It includes the formulation technology of the PSA and the manufacturing equipment. The blending ability of the components depends on their physical state and chemical composition. The chemical composition may influence their physical state as well. Solid or liquid components need different mixing equipment. Inert or reactive components must be mixed under different conditions. As discussed by Benedek in Ref. [8], blending of rubber–resin adhesives is carried out by wet or dry technology. According to the wet technology, the elastomer and the tackifier resin are dissolved. Their mixing occurs in the liquid phase. Wet blending of rubber–resin formulations generally includes a first solution step of the elastomers and a second dissolving step of the components. In dry blending the mixing of the components occurs in the solid/molten-phase, without dispersing agents or solvents. They are calendered together or mixed in the molten state.

10.1.1.1.1 Formulation Technology of Solvent-Based Adhesives

Formulation technology of solvent-based adhesives includes a premixing step and a mixing step. Solvent-based, two-component formulations that contain elastomers and tackifiers as the main formulating components require that the solid-state raw materials be micronized (cut or pelletized), mechanochemically destroyed (masticated, plasticized, etc.), and solubilized. In the first solubilization step the rubbery material is

transformed by conflation or mechanochemical destruction in an intermediate, which can be dissolved easily using common mixers.

In the first premixing step, the surface area of the solid raw materials (e.g., elastomers) should be increased by physical size reduction to facilitate dissolution. The dispersion process of agglomerated solids such as rubber, plastics, resins, or fillers is commonly carried out in internal mixers and continuous intensive mixers. The mixing effect is accomplished by repeated passage of the material through converging tight clearances, where it is exposed to high shear stresses.

Mechanochemical destruction is required for adhesives to be coated with a very low coating weight or to be cross-linked after coating. For instance, like recipes for tapes, most NR-based formulations for protective films use mastication by calendering to regulate viscosity and peel resistance. Because of the requirement for low peel resistance, a low coating weight is suggested for these products. Low coating weight can be exactly controlled by using low-viscosity formulations (see Section 10.2.2). Because of the low peel requirement, a relatively low level of tackifier resins is also recommended. A low level of tackifier resin means higher viscosity of the formulated adhesive (see also Chapter 8). The ratio of the viscosities of adhesive compositions based on unmilled/milled rubber is about 5–10, which means that, at least theoretically, low-viscosity rubber–resin solutions may be coated for protective films, although the resin concentration of such recipes is much lower than that for common label or tape formulations. Therefore, mastication plays a special role in the manufacture of adhesives for protective films. As a consequence, post-cross-linking (to increase the molecular weight) is very important (see also Chapter 1). In the second premixing step, the micronized components are solved or dispersed.

The dissolution process of certain elastomers imposes the prevention of gels. Unfortunately, cross-linking leads to a weighty increase in viscosity. A macrogel can be broken mechanically to yield a microgel. When a macrogel is broken, the active radicals can react internally to produce a more tightly cross-linked microgel, or they may react externally to give viscosity instability; therefore, the dissolution of styrene–butadiene–rubber is a difficult process. A microgel yields an easily dispersed, low-viscosity, smooth, shiny mastic; a macrogel gives a polydispersed, high-viscosity, grainy mastic. Macrogel formation can be prevented by improving rubber stability. Most of the viscosity increase occurs during the first few days of aging and depends on the solids level. The addition of aromatic solvents results in greater viscosity upon aging. Although a stable viscosity could be achieved through proper selection of solvent/resin/rubber level and total solids, the characteristics of the elastomer are the major determining factor in viscosity stability. In the mixing step, the solved or dispersed components of the recipe are mixed.

10.1.1.1.2 Recycling Technology of Solvent-Based Adhesives

Generally, recycling includes the recycling of the product's components (constructive components and technological components) and of PSPs [9,10]. The solvents used in solvent-based PSAs must be recycled or incinerated. Air cleaning for printing and coating requires the same technology. Recycling of solvents was described in detail in Refs [9,10]. This process can also include the solvent used for pre- or postfinishing of the pressure-sensitive laminate (e.g., with lacquers, primers, or printing inks;

see also Sections 10.2.2.3.2 and 10.2.2.3.3). Air recycling is related to solvent reuse or incineration. Exhaust and recycling must be adjustable as a function of the drying and of solvent concentrations.

10.1.1.2 Manufacture Equipment of Solvent-Based Adhesives

A preparation plant is necessary for the manufacture of the adhesive. Its complexity is a function of the nature of the adhesive to be manufactured.

Physical size reduction of the solid-state formulating components can be accomplished by using a bale chopper or granulator, a sheet mill and slab chopper, or a Banbury mixer. Milling equipment and their characteristics are listed comparatively in Ref. [11].

Dispersing or solving of the micronized components requires dissolvers. Low- and medium-viscosity rubber–resin solutions are manufactured in a vertical high-speed stirrer.

Mixing of the liquid-state components requires mixing equipment. Special formulating equipment is needed for cross-linked formulation, where curing of two-component adhesives (or primers) begins immediately after the components have been mixed together, and only a limited time (pot life) remains in which the adhesive can be applied. Mixers and dissolvers of the main suppliers are listed and examined comparatively according to their construction (type, material, etc.), functional characteristics (power, volume, rotations per minute, viscosity, working temperature, etc.), and suggested applications in Ref. [12]. Dry blending uses mixers working either discontinuously (in batches) or continuously (in extruder) [8].

Mixing of rubbers in an internal mixer is less well studied than processing on a two-roll mill. Mastication (on a calender) is the thermomechanical destruction and depolymerization of an elastomer. Mastication mechanism and mastication conditions for various elastomers were discussed in Ref. [8]. Calandering allows the application of the "dry" formulated blend by roll pressing on a porous web. This method was used mainly for the manufacture of medical tapes.

10.1.2 Manufacture of Water-Based Adhesives

The main differences between solvent-based and water-based systems are that solvent-based systems are homogeneous and water-based ones are heterogeneous; solvent-based systems have low molecular weight (limited by the solubility/viscosity of macromolecular compounds), whereas water-based ones possess higher molecular weight; solvent-based systems may be formulated without nonadhesive components, but water-based systems must include technological additives (see also Chapter 8).

Started with rubber–resin PSA solutions, label coating now uses mostly acrylic, water-based PSAs. Therefore, the formulation of PSAs for labels is mainly a formulation of water-based compounds. In practice, it consists of the blending of liquid-state components, that is, the viscoelastomer dispersion and the tackifier dispersion. It should be taken into account that in a different manner from true solutions, water-based dispersions have a limited (4-year) shelf life, narrow storage-temperature intervallum (−30 to +70°C), and low shear stability. The manufacture of water-based PSAs includes manufacturing technology and manufacturing equipment.

10.1.2.1 Manufacturing Technology of Water-Based Adhesives

Generally, formulation of water-based adhesives does not need a premixing (micronizing and dispersing/solving) step. The liquid-state components of the recipe can be mixed directly. If a two-component cross-linking water-based PSA is used, the mixing of components must be simple, and the proportions tolerance must be high. Pot life at the coating station must exceed 1 working day.

10.1.2.1.1 Formulation Technology of Water-Based Adhesives

The formulation technology of water-based PSAs is a mixing technology of liquids, with the exception of some special formulations in which molten resins are mixed with the water-based viscoelastomer dispersion (see also Chapter 8), or redispersible formulating components are used. Water-based adhesives are time-dependent, shear-sensitive, and temperature-sensitive systems that need special technological formulation, and their storage and transfer differ from that of solvent-based adhesives. Blending acrylic dispersions requires a test of compatibility, adjustment of pH, and, after the addition of solvent, plasticizers, or fillers, storage time. Peel improvement after longer storage times for a tackified acrylic dispersion is illustrated in Ref. [13]. Tackification of water-based dispersions with molten resin is discussed by Benedek in Ref. [14]. Blending of water-based emulsions is described by Foreman in Chapter 5.

10.1.2.1.2 Recycling Technology of Water-Based Adhesives

Recycling of water-based adhesives is focused on water recycling and waste removal of the solid-state components of the PSA. Recycling of the dispersant (solvent) of water-based formulations is a complex but classical technology. It includes the separation of the solid-state components, their incineration, and the purification of the water. Generally, the manufacturers of such dispersions supply the waste management technology for their products also.

10.1.2.2 Manufacturing Equipment of Water-Based Adhesives

The manufacture of water-based dispersions needs mixing and handling equipment. Water-based dispersions can be blended with common equipment used for liquid reagents. However, in the use of such equipment the temperature and shear sensitivity of dispersed systems should be taken into account. Storage tanks, pumps, filtering equipment, and pipelines are required. Mixing of a latex should be performed in a tank with a low-speed stirrer designed to minimize foam formation. Various types of pumps that are adequate for water-based dispersions are examined in Ref. [8]. According to Ref. [15], for the mixing equipment for dispersions the storage tanks are situated at a higher level to allow gravitational transfer. A multiple-paddle agitator and double helix with pitched blades are recommended. Such tanks have atmospheric communication via a formaldehyde solution closing system to avoid skinning and bacterial degradation. Excentrical barrel pumps with bypasses are used; such pumps can be washed with water after dosage; deionized water is suggested as diluting agent, a process viscometer is used, and pH regulation is made with stepwise dosages of ammoniac.

The priority of the addition of compounding ingredients (order of addition) is given as well. In some cases the formulation components (e.g., fillers, plasticizers, thickeners)

must be dispersed before they are added to the water-based dispersion. Agents for pH adjustment should be used as diluted. Grit (sedimented, agglomerated particles) formation during the storage and manufacture of water-based dispersions is discussed in detail in Ref. [8] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). Technical requirements for bulk storage tanks for water-based dispersions (e.g., material, vertical construction, gravitational transfer, stirring, humidification, disinfection, and cleaning equipment) are described by Benedek in Refs [1,4,8]. Various types of pumps are examined comparatively, according to their main characteristics and suppliers, in Ref. [16]. Solids content and the viscosity of water-based acrylics versus ethylene–vinyl acetate copolymer (EVAc) and carboxylated butadiene rubber (CSBR) PSAs are listed by Benedek in Ref. [13].

10.1.3 Manufacture of Hot-Melt Adhesives

Hot melts are based on special designed polymers that need complex formulation. Generally, hot-melt PSAs (HMPSAs) are formulated from thermoplastic elastomers (TPEs) and viscous (liquid) components (see also Chapters 3 and 8). Their manufacture includes the technology and manufacturing equipment.

10.1.3.1 Manufacturing Technology of Hot-Melt Adhesives

The manufacture of HMPSAs requires mechanical size reduction, micronization of certain elastomers (TPEs are generally pelletized), and molten state mixing of them with other components of the recipe (tackifiers, oils, antioxidants, etc.). Such mixing is carried out discontinuously or continuously [4,8] with a special apparatus that produces a heat history of the material. For continuous mixers the heat history is very low. Principally, melt mixing can be carried out using a variety of heated mixing equipment. In order of increasing effectiveness, these include vessels stirred with propellers, vessels with high shear (Cowles type) dispersers, planetary mixers, internal mixers (Sigma blade or Banbury type), and modifications of these. In low-shear mixers, resins, plasticizers, and stabilizers should be melted first and thermoplastic rubber crumb added incrementally. Where production rates are high enough, continuous mixers are desirable because they reduce degradation of the rubbery mid-block.

10.1.3.2 Manufacturing Equipment of Hot-Melt Adhesives

Thermoplastic elastomers used for hot melts are more degradation sensitive than NR. Therefore, principally, wet and dry mixing of hot-melt components is possible. Wet (solvent-based) blending and coating eliminates the effects of both thermal history and mixer shear on the compatibility of the components and subsequent adhesive performance. On the other hand, solvent blending may lead to a difference in morphology due to difference in the rate of solvent removal as a function of adhesive thickness [17]. Industrially, dry blending is carried out, whereas solvent blending is used in the laboratory only [18]. Readers interested in the effects of processing (solvent-based vs melt blending, solvent-based vs melt coating) on the adhesive properties of PSAs are referred to the work of O'Connor and Macosko [17] and Kim et al. [19].

For hot-melt manufacture, compounding is mixing of the adhesive components at 120 and 200°C, where the shear forces cause a drop in the viscosity. The construction and hydrodynamic characteristics of the mixing equipment may influence the processing performances of HMPSAs; the raw materials used affect it also. For instance, when polyacrylate rubber-based HMPSAs are prepared, high shear mixing is required. As a rule of thumb, increasing mixer shear and temperature lead to better mixing of the adhesive components, a breakdown in molecular weight, and a subsequent increase in tack and reduction in shear performance. In some cases, these effects may be significant enough to overwhelm any effects caused by changing the adhesive formulation; for that reason, some researchers choose to solvent blend and solvent coat samples rather than use a mechanical mixer or extruder. Furthermore, adhesive melt viscosity and shear strength are extremely sensitive to melt processing and subsequent breakdown in molecular weight, whereas tack and peel resistance are relatively robust and will remain relatively unchanged [18]. Hot-melt formulation machines and processing machines exist.

For hot-melt formulation continuous or discontinuous mixing is carried out with various high-shear mixers, such as *Z*-blade or sigma-blade mixers, inert gas blanketed or vacuum operating, jacketed, heavy duty mixers, cavity mixers, or extruders. According to Ref. [20], the following equipment is suggested for manufacture of hot melts: single-screw extruder, twin-screw extruder, corotating, counterrotating, tight intermeshing or tangential, planetary extruder, and cokneaders. Continuous, high-shear mixing uses 1,000–2,000 s^{-1} shear rate; batch-wise medium-shear mixing works with 100–200 s^{-1} shear rate, and batch-wise low-shear mixing uses shear rates lower than 100 s^{-1} shear rate. The temperature at which mixing occurs, rather than the level of shear, is the primary factor affecting degradation.

Discontinuous mixing uses equipments that are common in processing of rubber; continuous mixing is extruder based, like the processing of plastics. In the continuous processing of HMPSAs a relationship exists between plug diameter and melt viscosity; melt viscosity decreases with plug diameter. The order of addition of various components of the recipe depends on the recipe. Continuous mixers exhibit the advantage of excluding air, reducing mixing times, and operating with higher viscosity. For instance, the residence time for a continuous extruder is 2–6 min with a production of 800–200 kg/h and viscosity of 120 Pa · s at 175°C (formulation based on Cariflex 1107, resin, and oil). Various constructions of extruders (mono-screw, twin-screw, and intermeshing twin-screw) are described by Benedek in Ref. [8]; their productivity and costs are compared with that of discontinuous mixers. Auxiliary equipment (e.g., for melting and metering) is described as well. For continuous mixing and granulating, hot-melt extruders with underwater solidification and cutters are generally used. Cast, strand-granulation, and rotoforming (drop) equipment are also used. A production line for continuous compounding of HMPSA is described by Benedek in Ref. [13].

Yelin [20] described continuous hot-melt production in a twin-screw extruder. The main advantages of this technology include the short time to be ready for production (the final product is manufactured just 5 minutes after the extruder is started); no cleaning is needed before a change of recipe, and no thermal degradation appears due to the short residence time. Large-volume twin-screw extruders are presented, and examples of continuous hot-melt production for various PSPs are listed. Tackifier addition in a

twin-screw extruder with a cooled twin-screw side-feeder is discussed. The development of extruders leads to machines with greater volume, large screw volumes, and deep screw channels. For PSA recipes such extruders allow mastication and plastification of the elastomer, melting and homogenization of the resin, homogenization of the plasticizer, dispersion and devolatilization of the fillers, and homogenization of the stabilizers. Such a machine for PSAs has a throughput of about 1.4 t/h. A flow chart for the manufacture of transdermal therapeutic systems (based on HMPSAs compounded in an extruder) is presented.

Hot-melt processing machines prepare the hot melt for coating. For this process, a melt tank with premelting grid and gear pump, a combination of drum-melter/metering system, an extruder, or an extruder in combination with a metering pump were suggested (see also Section 10.2.2.1.2).

10.2 Manufacture of Pressure-Sensitive Products

Generally, the manufacture of PSPs includes the manufacture of solid-state components (e.g., carrier materials for face stock and for release liner), the manufacture of liquid adhesive and nonadhesive components (e.g., PSA, release, primer), and their assembly in a continuous web-like material. The PSA can be coated on or built into the bulk carrier material. The classic way to manufacture a PSP is by coating a carrier material with a PSA. Manufacture of the finished product by carrier coating employs a coating technology completed by other converting steps that are common for web-like products (see also Section 10.3). For some products, laminating after coating is required as well. Generally, coated adhesives are components that are deposited on the surface of a carrier material. As discussed later (see Section 10.2.2), there are various coating methods depending on the adhesive, the carrier material, and end-use requirements. Built-in adhesives are chemical compounds that can be mixed in with the components of the carrier material and processed as a homogeneous or heterogeneous (i.e., laminate) composite. Such adhesives are processed together with the main thermoplastic component of the carrier material and, therefore, no supplemental adhesive coating is necessary (see also *Applications of Pressure-Sensitive Products*, Chapter 7).

As discussed in Chapter 8, other liquid components (e.g., primer, antistatic agent, lacquer, release) can be coated on the solid-state components (carrier and release liner) of the PSP. Simultaneous manufacture of the PSA and pressure-sensitive laminate has been described [13].

10.2.1 Manufacture of Other Web-Like Components

The manufacture of other liquid components to be coated includes the manufacture of the release coating and other components required for the pre- or postcoating of the web (see also Chapter 8). Manufacture of the release coating was discussed in detail by Benedek in Refs [1,9]. Developments in this special domain of polymer synthesis and formulation are discussed by Schmidt and Jones in Chapter 9. Manufacture of the release liner by coating was described by Benedek in Ref. [13]. Manufacture of various

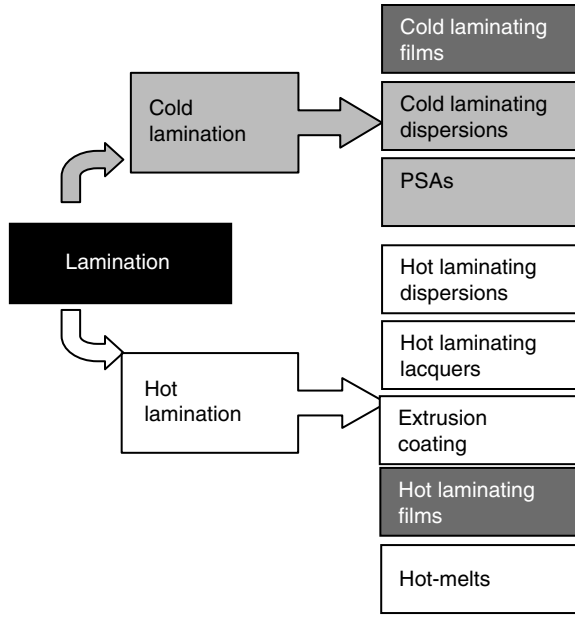


FIGURE 10.1 Special domains of lamination technology.

(nonadhesive) coating components was also described in Ref. [13]. Their range comprises primers, printing inks, antistatic agents, etc. (see Chapter 8).

10.2.2 Web Finishing

Web finishing is the coating of liquid product components on solid-state web components or their build into solid-state web components. From the technological point of view, PSPs can be manufactured using coating, extrusion coating, or coextrusion. Each of these methods exhibits advantages and disadvantages (see also Table 10.1). Therefore, their applicability for a given product must be rigorously examined.

As illustrated by Figure 10.1, pressure-sensitive lamination is a special case of cold lamination. The manufacture of PSPs by adhesive coating and laminating has some of the general advantages of adhesive lamination such as simplicity of the line, the potential to laminate any preformed web, lay flat when the web tensions are under control, minimum make-ready times, and no extra material wastes for caliper adjustment, edge bead, etc.

10.2.2.1 Manufacture of Pressure-Sensitive Products by Coating

The manufacture of PSPs by coating is a common procedure for classic products. The manufacture of pressure-sensitive labels by coating was described by Benedek in Ref. [9]. Build-in of the adhesive in the carrier is a practice used to manufacture virtually adhesive-free self-adhesive products (see *Applications of Pressure-Sensitive Products*, Chapter 7). The manufacture of PSPs by coating includes the coating technology and the coating equipment.

10.2.2.1.1 Coating Technology

Coating and printing technology are used for the manufacture of finished products by coating. Coating as a technology is less complex than printing. Coating technology uses various coating methods; their choice depends on the physical state of the adhesive (e.g., solvent-based, water-based, or HMPSA) and PSP grade. Coating methods used for the main PSPs are discussed by Benedek in Ref. [1]. For labels, roll-coating and screen printing offer the best results, but blade, cast, and slot-die coating are used also. For tapes, roll-coating, slot-die coating, extrusion, and calendering are mostly used, but blade, cast, and spray coating were suggested as well. Protection films are manufactured by roll and blade coating.

The coating technology and coating machines were described by Benedek in Ref. [9], along with coating systems/devices, which were discussed in detail. In this chapter, only their special product-related features will be described. The main coating methods for liquid materials are based on cast, spraying, roll, blade, and screen-printing techniques, but calendering has been used as well. Coating methods can be classified as impact (i.e., contact) coating (e.g., roll-coating, screen printing) and nonimpact coating (e.g., spray coating, curtain coating) and according to the dosage of the coated material, that is, whether it is in excess or metered (see Table 10.2).

The main aspects of coating technology refers to direct or transfer coating, mono- or multilayer coating, and in-line- or off-line-coating. Coating technology is a function of carrier, adhesive nature, and end-use properties of the laminate. Coating technology is generally a function of the product class (label, tape, etc.), which, as discussed earlier in Chapter 8, imposes the formulation of the adhesive. For instance, because of the special role of the face stock material as an information carrier and the high surface quality required for labels, only classic coating technologies using very fluid adhesive and yielding a smooth adhesive surface are suggested for label manufacture. Taking into account the balanced adhesive properties required for labels (see also Chapter 8), with the exception of some low-cost products, the majority of labels are manufactured with

TABLE 10.2 Working Principle of Various Coating Devices

Impact Coating		Nonimpact Coating	
With Adhesive Excess	With Adhesive Dosage	With Adhesive Excess	With Adhesive Dosage
Knife coating	Slot-die[c]	Air brush[f]	Spray coating[d,f]
Roll coating[a]	—	—	Curtain coating[e]
Screen coating[a]	—	—	—
Calendering[b,c]	—	—	—
Main use in other technologies*			

[a] Printing (gravure, flexo).
[b] Rubber processing.
[c] Plastic film manufacture (cast, chill-roll film).
[d] Printing (ink jet).
[e] Plastic film manufacture (plasticized cast film).
[f] Lacquering.

water-based or solvent-based adhesives. Label manufacture is generally the coating of a medium (15–25 μm) dry adhesive layer with a very smooth image on a nontextured, smooth carrier surface and lamination of the adhesive-coated web with the release liner (direct coating) or with the final face stock material (transfer coating). For special products requiring a very smooth adhesive layer, direct coating possesses the advantage that, by its application, air bubbles are avoided. On the other hand, for PSPs with storage and material transfer function (e.g., transdermal drug delivery systems), transfer coating is preferred (see Chapter 7).

Coating of 100% solids (hot melts and radiation-curable oligomers) requires adequate technology. A special feature of radiation cross-linking is its anisotropy. The radiation is partially absorbed, partially transmitted, and reflected; the maximum radiation level is given at the top of the adhesive layer. That means that the cross-linking degree is at the maximum on this side. Therefore, in this case, direct and transfer coating yield different adhesive characteristics.

The choice of direct or transfer coating depends on the carrier material. Its environmental sensitivity or thermal sensitivity (e.g., film carrier) may impose the use of transfer coating for solvent-based or hot-melt-based PSAs. Porous- or heat-sensitive face stocks require the use of transfer coating, and coating of fabric is carried out using a transfer procedure. Hot melts are limited by their low heat resistance, low penetration into porous substrates, and relatively high application temperatures of 150 to 200°C. Even at these application temperatures, some hot melts are highly viscous (which affects their ability to be coated with very low coating weights) and can cause damage to sensitive substrates.

Such a chemical or thermal sensitivity of the carrier or wetting or anchorage problems may require the use of multilayer coatings (e.g., primer–PSA, PSA–lacquer, lacquer–printing ink) on the carrier material or release liner (one-side-coated or double-side-coated), but product build-up and application may force multiple coating as well (see *Applications of Pressure-Sensitive Products*, Chapter 1). The adhesive can also have a multilayer structure. Such a structure may control creep compliance, with a plurality of superimposed adhesive layers with different gradients of shear creep compliance. The heterogeneous multilayer adhesive can be manufactured by UV-light-induced cross-linking of 100% solids acrylics where direct and transfer coating yield different adhesive characteristics. The maximum radiation level is experienced at the top of the adhesive layer; therefore, the cross-linking degree is at a maximum on this side.

The finished pressure-sensitive web may include one or multiple solid-state components (see also *Applications of Pressure-Sensitive Products*, Chapter 1), which can be coated simultaneously (in-line) with the same coating/laminating machine or off-line and then laminated together. Therefore, such products influence the complexity of the coating machine. Printers can siliconize and adhesive coat in their own plant and save as much as one third of their manufacture costs. In-line siliconizing combined with HMPSA coating was developed 2 decades ago and offers economic advantages. Processing of HMPSA is influenced by the parameters of viscosity, coating speed, and coating weight.

Economic considerations forced the in-line manufacture of PSPs. Production equipment has been developed for simultaneous adhesive/abhesive coating and lamination. In-line extrusion and coating of film-based PSPs is also possible. As summarized by

Benedek in Ref. [1], this procedure offers the advantages that treatment exists, no supplementary technical operations (e.g., handling and maintenance) are required, the own carrier material is used, and the global know-how is protected. On the other hand, time-dependent postmanufacture processes work in the film and change its surface quality and geometry, the coating speed is lower, and such manufacturing uses a mixed technology.

Protective films are coated with 0.5–3.5 g/m^2. Similar low coating weights of a cross-linking adhesive are used in laminating also. Coating weights of 0.8–1.5 g/m^2 are used for laminating of smooth surfaces, 1.2–1.8 g/m^2 for printed films, and 3.5–4.5 g/m^2 for paper laminates. Therefore, at least theoretically, the coating technology of protective films is related to the well-known procedure used for laminating films. Its choice depends on the nature of the adhesive, its coating weight and geometry, the carrier nature and geometry, and the end-use of the product.

The transition from solvent-based adhesive to water-based PSA has not been simple. The low mechanical stability of water-based adhesives (manifested by coagulum build-up and foaming) in comparison to solvent-based adhesives imposes the use of adequate coating devices (see later). Water-based systems are more efficiently dried by utilization of air volume rather than air temperature; therefore, they need special coating/drying equipment (see later).

The choice of a coating technology strongly depends on the coating weight. Common coating weight values used for tapes (5–40 g/m^2) are listed by Benedek in Ref. [1]. Generally, the coating technology of tapes uses multiple coatings of the carrier (face and backside) with different (primer, adhesive, and abhesive) layers, and cross-linking of the adhesive coated with higher coating weights is a general feature of tape manufacture. For instance, the coater of double-side tapes uses both the transfer- and the direct-coating methods. The first coating station deposits the adhesive on the release liner (transfer coating). In a combining nip, the adhesive-coated release liner is sandwiched with the carrier material (lamination). The duplex structure then proceeds to the second coating station, where a second adhesive layer is applied on the carrier material (direct coating).

The chemical composition of the adhesive and its formulation determine its coating rheology (i.e., dispersed or 100% solids) and affect the coating technology. For instance, thermoplastic elastomers are coated as hot melts and acrylics can be coated as solvent-based or water-based formulations, but acrylic hot melts and radiation-cured compositions are also known (see also Chapter 8). The diversity of radiation-curable formulations (and their coating rheology) depends on the radiation used and on the monomer–oligomer- or macromer-based formulation. For instance, 100% acrylics can be coated as low-viscosity monomers, medium-viscosity oligomers, or high-viscosity hot melts using postcuring technology. Considering their versatility for acrylic prepolymer-based adhesives with different viscosities, the coating lines can be split into the following ranges: equipment for a viscosity of less than 500 Pa · s, 200–2,000 Pa · s, and 500 to 5,000 Pa · s.

10.2.2.1.2 Coating Equipment

Coating equipment includes the coating machine, coating devices, and auxiliary equipment. Various application domains for the main PSPs (e.g., labels, tapes, or

protective webs) forced the development of various products (see *Applications of Pressure-Sensitive Products*, Chapters 1 and 7). Their complex construction requires the use of different coating machines and coating devices.

Coating Machines Processing lines are designed for the companies' purposes and combine individual units of various mechanical engineering suppliers. Their choice depends on technical and economic considerations. Technical considerations include the product complexity (components and build-up) and its postprocessing (converting and confectioning). Coating machines for direct and transfer coating, a classic tandem machine for label manufacture, a coating machine for primer and adhesive coating, and an in-line coating-laminating plant were described by Benedek in Ref. [9]. The main components of a coating machine for solvent-based, water-based, and HMPSAs are also discussed.

The main processes in the self-adhesive coating and lamination are web handling, coating, drying and curing, and moisturizing. The major coating machines include web-pretreating and posttreating equipment and are designed for in-line production (e.g., release coating/corona treatment/priming/PSA coating; or corona treatment/priming PSA); for very thin coatings, such as solventless silicones (such systems have problems with broad webs at high running speeds); for medical products like in-line- and tandem-coating with solvent-based and water-based PSAs, on soft PVC carriers or nonwoven fabric and paper carriers; for crêpe-paper coating (such systems are strongly influenced by the pleating degree of the paper); for high coating weight on a textile carrier; for wetting-out of difficult carrier materials; for labels (e.g., for smooth, coated layer, rough carrier surface, nonuniform carrier profile); for protective films (with a broad and thin, deformable, carrier web; and for rubber–resin PSAs with high solids content. Coating of soft, tension-sensitive polyvinyl chloride (PVC) carrier materials requires a relaxation station on the coating machine.

Generally, the following parameters are determinant concerning the versatility of coating equipment to produce PSPs belonging to different product classes: the ability of the coating device to process PSAs of different physical state with different coating geometry, the on-line slitting and cutting possibilities, the existence of lamination equipment, the possibility of in-line flexoprinting, and the possibility of in-line release coating.

As discussed previously (see Section 10.1.2.1.1), product build-up (the nature, number of components, and construction of the PSP laminate) influences coating technology. Details concerning the laminate components and the build-up of the laminate are discussed in *Applications of Pressure-Sensitive Products*, Chapters 1 through 7. For products with a multiweb structure, multiple coating is required. For such products the different coating steps can be carried out with different coating methods and devices. For instance, for a label the PSA, the release agent, the primer, and the lacquer can be coated using different coating methods. However, if possible, the same aqueous or hot-melt-based technology should be used for different coating operations (e.g., primer and adhesive coating or release and adhesive coating). Labels use a separate release liner sheet that is normally applied in a single pass. Label stock manufactured on a one-station coater might require two or three passes to complete the process of applying a primer,

adhesive, and laminate. Two- or three-station coaters would perform all of these operations in a single pass. Such multiple-station coaters deposit three or more coatings on one or more carrier materials in a single machine pass.

Roll-fed coaters and sheet-fed coaters are used. Sheet-feed printing presses have the ability to print variable size images on any sheet size. Sheet-feed coaters can apply a top or bottom coating. The usual width of the coating machines (70, 100, 140, and 200 cm) is given by the 70 × 100 cm sheet formate.

The common manufacturing procedure of tapes includes in-line priming, release layer coating, and adhesive coating. Primer and release coatings can be dried in either vertical or horizontal ovens. The solvent-based technique is the most proven and popular technology for the production of tapes. The development of tapes started with rubber–resin-based formulations. Tape manufacture can require the in-line double-side coating of the carrier. For instance, a release coating (0.2 g/m^2) is applied on the bottom side, and a primer (1 g/m^2) is coated on the top of the carrier. In this case, gravure coating is recommended (see later), but two smooth rollers or reverse gravure can be applied as well.

In the manufacture of protective webs, depending on the roughness of the product surface and laminating, delaminating, and processing conditions, chemically different adhesives are applied with different coating weights on various, mainly film, carriers using various coating devices. The mean nominal coating weight values are situated between 1.5 and 7.0 g/m^2. For low coating weight values plus tolerances are preferred.

For coating of solvent-based adhesives a surface tension higher than 38 mN/m and for aqueous formulations a tension higher than 46 mN/m is necessary. High-solids solvent-based acrylics have solids content higher than 60%. For instance, a PSA with 65% solids content has a viscosity (Brookfield) of 15,000 mPa · s (at 25°C). The viscosity of common acrylic dispersions is listed in Ref. [4].

The influence of the formulation on drying was discussed in detail by Benedek in Ref. [4]. Drying as a diffusion-related phenomenon, mathematicized by Kundsen's and Gardner's equation, Sherwood's and Reynold's invariant, and Schmidt's number, was discussed comparatively for solvent-based and water-based adhesives. Drying methods (e.g., thermal convection, infrared, radiofrequency, and UV and EB drying) and equipment were described by Benedek in Ref. [13]. Various drying tunnel constructions (e.g., with rollers and air jets over the web, with rollers and air jets over and under the web, with rollers and conveyor belt and with air flotation) were presented. Drying speed is influenced by the adhesive nature and formulation (see Chapter 8). Water-based PSAs require stand-alone equipment, space for a drying channel, and remoisturizing. Equipment and energy costs are much higher for such adhesives compared with HMPSA coating, although the production capacity is higher. For water-based adhesives the relative humidity of the air is the main parameter of drying. For water-based coatings the drying capacity must be increased to provide the extra energy required to evaporate water versus solvent. This is difficult to achieve without extending the length of dryers, reducing the drying speed, and affecting the printing register, a critical point when coating plastic webs. On the other hand, the same drying channel is frequently used to handle both solvent-based and water-based adhesives.

Different adhesives need different drying temperatures. For instance, the drying temperature recommended for a thermoplastic adhesive is about 200°C, thermosetting adhesives need 250°C, self-cross-linking adhesives require 200°C, and emulsion-based adhesives are dried at about 210°C.

If multiple layers are coated with different dispersing media, the build-up of the drying equipment may be complex. For instance, for drying of an in-line-coated double-side tape (with release and primer), because of the different solvents and coating weights applied, two different drying units are suggested. A tangential air-jet dryer was recommended for drying of the release layer and an air-jet with a longer channel for the primer. Drying equipment and suppliers are listed and examined comparatively in Ref. [21].

Infrared (IR) drying offers the possibility of regulating the drying intensity in the cross-direction; it is characterized by low space requirements and can be used as intermediate drying between coating and printing devices. Combined IR/air drying gives better results.

The main parameters of the wet-film quality (Q_{wc}) for solvent-based PSAs include surface tension (γ), solids content (S_a), viscosity (η), solvent characteristics (N_s), and temperature (T) [4].

$$Q_{wc} = f(\gamma, S_a, \eta, N_s, T) \tag{10.1}$$

The quality of the dry coating (Q_{dc}) depends on the evaporation rate of the solvent (R_{es}), which is a function of the coating thickness, that is, coating weight (C_w), solids content of the adhesive (S_a), solvent characteristics (N_s), and drying conditions (C_d).

$$Q_{wc} = f(C_w, S_a, N_s, R_{es}) \tag{10.2}$$

The use of solvent-based adhesives imposes the removal of organic solvents during drying and a special solvent-recovery system (see later). Exhaust and recycling must be adjustable as a function of drying and solvent concentrations. For instance, a classic machine for adhesive tapes for cardboard sealing, designed for a production speed of 350/min, uses a solvent-based PSA with a coating weight of 20 g/m^2 (solids content of 28%) and a solvent mixture of hexane (70%) and toluene (30%) and a carrier of oriented polypropylene (OPP) of about 40 μm.

Hot-melt coating machines can coat paper, fabric, poly(VAc), and polyester films. Hot-melt coatings can be defined as those thermoplastic coatings that have a minimum viscosity of 9,000 mPa · s. Hot-melt coaters can utilize a carrier preheating drum to improve the adhesion of the HMPSA and its surface profile. In such melt-mill coaters the adhesive is exposed to air [4]. The most HMPSA coating machines for labels are intended for continuous coating of 18–24 g/m^2. Such machines possess an in-line filter with a filter cartridge and replaceable coating heads. By inserting various shim plates and Teflon profiles, operators can change the application width and pattern. Ulman and Thomas summarized the benefits and technology of hot-melt adhesives in health care applications [22]. They pointed out the side benefit of being able to use less expensive and more energy-efficient coating equipment and being able to more easily coat adhesives in thick sections without the bubbling caused by solvent evaporation in solvent-borne systems. In the coating of HMPSAs, their high specific heat and low thermal conductivity

must be taken into account. For instance, styrene block copolymers need three times more melting energy than EVAc copolymers. Coating of HMPSA supposes the existence of premelters, melt tanks, melt extruders, filters, feeding lines, pumps, and heating systems (see Section 10.1.2). Such systems are described in a detailed manner in Ref. [1]. For label coating with HMPSAs a drum-melt system ("melt-on demand") is usually applied. In this case the coating device includes a melt supply, coating slot die, gear pump, temperature controllers, metering bar (see later), back-up roll, chill roll, and tension control.

On modern machines the coating head automatically swivels away from the substrate if the unit stops. Laminating rolls mounted to the side of the coating cylinder are either cooled or heated to maintain an accurate finish and coating weight.

By analyzing the changes that occurred in the domain of pressure-sensitive technology one can note that line speed and web width increased, adhesive thickness measurement and feedback became the standard, multitechnology combined machines were available, and changeover time had been reduced. Developments in machine design include an unwinder with fully automatic reel changeovers at top line speed, with a very short and constant overlapping tail; preconditioning rolls with tension nips, in-line flame treater, release coating unit with total solvent capture, air flotation dryer, a coating device with slot-orifice-die with automatic adhesive thickness control, and a rewinder with independently indexing arms, allowing changeover at full speed. The diversification of coating equipment is illustrated by Werner [23]; a pilot coating machine with web width of 400–1,300 mm, web speed of 5–1,600 m/min, and flying splice winding can use 60 various coating methods, 5 coating modules, gravure coating with a chambered blade, and a curtain coater.

Coating Devices/Coating Systems Various constructions were developed for coating devices. From a theoretical point of view, a coating device (system) is based on a knife (known also as a blade, doctor blade, bar, Meyer bar), a rotating cylinder, or a slot die. These components can have very different constructions. Both the metering knife and the metering roll can be placed on the roll or on the web. For instance, an adhesive applicator apparatus for (low- and medium-viscosity) liquid adhesive includes a rotating applicator cylinder, an adhesive tank for the supply of the adhesive to the cylinder, and at least one doctor blade operatively associated with the applicator cylinder. Coating devices and the choice of the coating geometry were discussed by Benedek in Ref. [9]. As noted, the desired coating weight range, viscosity, changes in coating weight, abrasion of metering devices, changes in coating (web) width, and changes in coating medium are the most important parameters that influence the choice of coating geometry. The main parameter affecting the choice of coating device is the rheologic behavior of the adhesive. It is well known from the practice of laminating that adhesives with different flow characteristics require different coating devices. The influence of the environmental and experimental conditions on the rheologic properties (e.g., viscosity range, shear thinning) of the uncoated, liquid PSAs was discussed in detail by Benedek in Ref. [3], where the rheology of PSA solutions, its special features (e.g., polymer- and solvent-dependent characteristics, technology-dependent characteristics, and adherend-dependent characteristics) were described. The rheology of PSA dispersions (viscosity, wet-out, and their mutual influence) was also discussed.

Different coating devices, such as direct gravure, offset gravure, reverse roll, and knife over roll, can be used. Generally, the coating devices differ according to the principle of

coating (how the liquid adhesive mass is transformed in a stable, thin, solid-like layer) and the construction details of the coating device. Principally, coating devices can be divided into devices with web contact and contactless coating methods. They can be classified as follows [13]: direct-transfer metering by knife over roll; direct-transfer metering by slow, rotating roll knife (roll-blade coater, knife over web on the roll); direct transfer knife over the web; kiss coating–premetering by knife or reverse roll; direct transfer, knife on the web, and air knife; multiroll coating (in a direct sense)–premetering in the direct or reverse sense; reverse roll coating–premetering by knife over roll or reverse roll; direct transfer with slot-die (slot-orifice) working like an extruder.

Advances in raw material development caused important changes in coating technology and forced the improvement of coating devices. The most common coating systems are cartridge-style coaters.

Choice of Coating Device/Coating Station The choice of coating device depends on the product class (label, tape, protective web, etc.) and on the physical state of the adhesive (e.g., solvent-based, water-based, or hot melt). Each product class requires a given coating weight and coating image (geometry and surface quality). Both depend on the rheology of the liquid (molten, dispersed, or solved adhesive) and its running performance characteristics (see Chapter 8). Continuous or discontinuous smooth or structured adhesive layers are coated as a function of the end-use performance characteristics of the PSP. Rigid, thick, and uneven surface materials are usually coated on sheet-fed curtain coaters or spray coaters (see later). Pattern coating can be carried out using special flexible chablones. Thus, full-width, stripped, beaded, spot, patterned, or zoned coating is possible. An embossed coating cylinder can coat a PSA in a pattern on a paper carrier material. For coating of a high-gloss adhesive layer on film carrier materials, rotating bars can be used to eliminate streaks.

Different adhesives and coating methods give different coating images. For instance, cross-linked adhesives with limited fluidity (because of their gelling) can lead to quite different coating images by use of various coating devices and, thus, to different geometries of the PSA layer for the same application domain. Thus, the same grade of protective film manufactured with various coating devices possesses different coating weights and coating geometry (but can exhibit the same application characteristics). On the other hand, the same type of coating device with different characteristics (e.g., Meyer bar number) may lead to higher coating weights (as usual) and much higher adhesion build-up (see *Applications of Pressure-Sensitive Products*, Chapter 8).

The influence of the formulation on the coatability of solvent-based, water-based, and hot-melt adhesives was examined comparatively by Benedek in Ref. [4]. As discussed previously (see Chapter 8), the viscosity of the adhesive depends on its formulation. For instance, rubber-based conventional hot melts exhibit a viscosity range situated between 10,000 and 60,000 mPa · s. Rubber-based EB-curing hot melts have a viscosity range of 20,000–100,000 mPa · s; acrylate-based EB- or UV-cured systems possess lower viscosities, at 10,000–30,000 mPa · s at 120–170°C. For low viscosities (e.g., 100 P) roll-coating (coaters with 2–4 metering and application rolls) is suggested; for higher viscosities (350–5,000 P) slot-die coating is suggested. It should be mentioned that the data of the literature concerning the usability limits (viscosity) of various coating methods are very

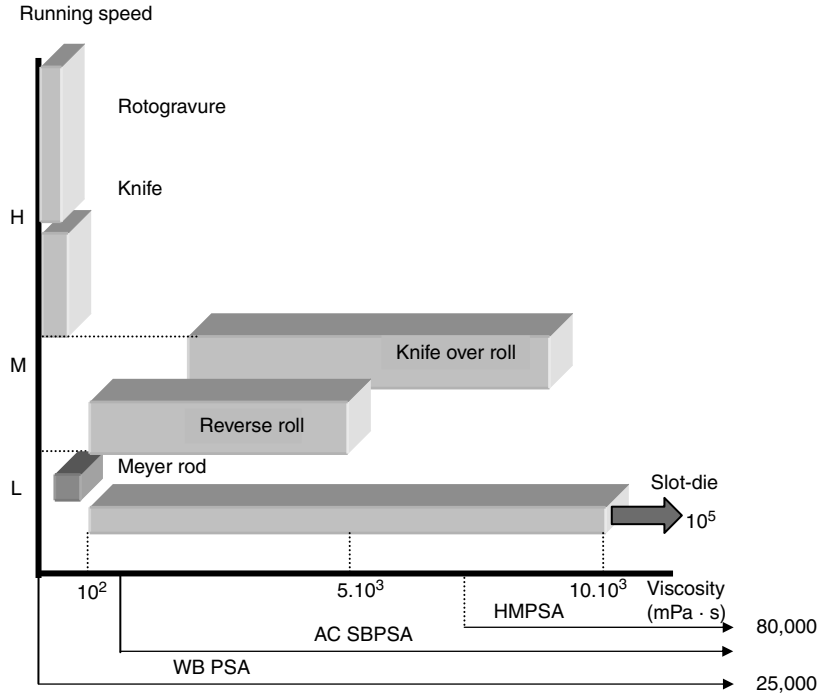


FIGURE 10.2 Viscosity domains of various coating devices.

contradictory (see Figure 10.2). On the other hand, taking into account the very different coating weight values for various PSPs (see Figure 10.3), it is evident that quite different coating devices are suggested for labels, tapes, or protection films.

Contactless coating methods for HMPSAs were developed to allow the use of hot-spray technology for the nonwoven market. First stripes, dots, or full-surface coating of HMPSAs was possible. By spraying larger surfaces, temperature-sensitive materials can also be coated. Controlled fiberization was introduced in 1986. Such a system uses a set of air jets to orientate the bead of adhesive, drawing it down in to a fine fiber applied in a helix-like pattern. Spiraling the adhesive maintains good edge control, even in intermittent applications up to 33/m/min. The spiraling also cools the adhesive, permitting applications of hot melt on heat-sensitive substrates. A recent trend for hot melt is the use of closed systems. Nozzle technology with electromagnetic valves, melt blow process, and controlled fiberization are noncontact applications that were developed [24]. Hot-melt coating systems are described in detail by Benedek in Ref. [13].

Radiation-curable systems can have different compositions and viscosities. As discussed previously (see also Chapter 1), coating of UV-curable formulations was developed from coating of monomer mixtures. Generally, a radiation (UV and EB)-curable, monomer-based formulation includes a hard monomer system, a soft monomer system, and multifunctional monomers. Such low-viscosity formulations require quite

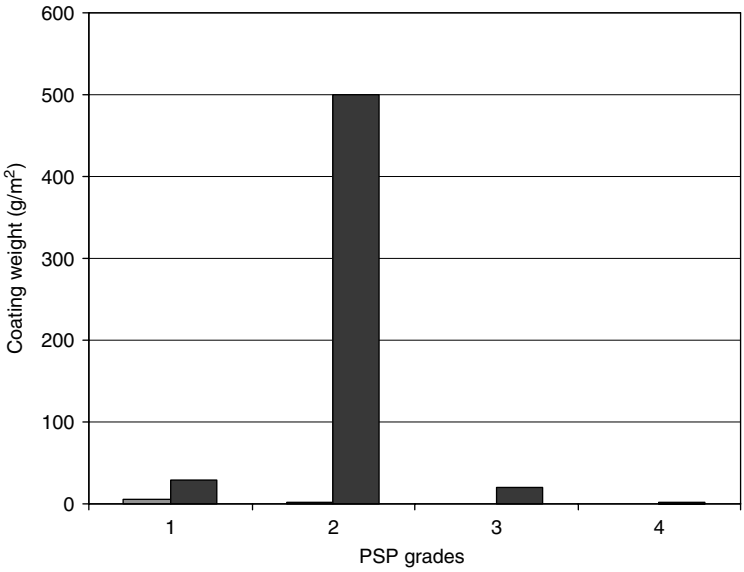


FIGURE 10.3 Coating weight values (minimum–maximum) for various PSP grades (1) labels, (2) tapes (3), protection films, and (4) separation films.

different coating technology in comparison with the coating of oligomer/macromer-based recipes. Uniform, isotropic adhesive layer can be achieved using an UV-transparent face stock (backing) and double-side irradiation. The manufacturing of such UV-cross-linkable acrylates is more expensive than that of acrylic dispersions. However, they are an alternative to solvent-based adhesives; a common hot-melt processing line can be equipped with UV-curing lamps without too much capital investment. The coatability of prepolymer-based formulations is discussed in Ref. [4].

The manufacture of release liner by coating involves a complex chemistry and great precision in coating of very low coating weights using gravure or flexoanilox rolls. The in-house choice is between solventless thermal and radiation-cured release agent. The manufacture of release liner and coating machines for release liner were described by Benedek in Ref. [9].

Very low coating weights for protective films can be coated with a four-cylinder nip-feed coating device.

In contact coating the adhesive is coated on the web by means of a device with mechanical contact to the web. In contactless coating the adhesive is transferred on the carrier web without a mechanical contacting part, that is, as a free material stream. The main contact-coating methods are variances of processing methods used in the printing industry (e.g., blade coating, roll coating, screen printing) and in the extrusion processing of plastics (e.g., slot-die coating). Contactless coating includes spraying, air knife, curtain coating, etc. First, the contact-based coating devices will be briefly described. They differ according to their construction; the adhesive is transferred to the web by a rotating unit (roll) or by an orifice (die) and metered by knife or roll constructions. Thus, blade coaters are roll coaters also. The working characteristics of various coating devices are listed in Table 10.3.

TABLE 10.3 Working Characteristics of Various Coating Devices

Coating Device	Viscosity (Pa · s)	Coating Weight (g/m^2)	Coat Weight Tolerance (%)	Speed (m/min)	Foam (%)	Notes	Suggested PSP
Meyer rod	0.3–0.8	2–50	10–20	150	10–20	Easy PSA and	R, PF
Chambered	–	–	–	–	–	web width	
Doctor blade	–	–	–	–	–	changes	
Knife over roll	4–8	–	–	200	10–30		T
Direct roll	100	–	5	–	–	For short run;	
3–4 roll	0.2–150	16–100	–	400	–	easy changes	PF
3 roll	15 HMPSA	–	–	–	–		
Nip feed	1–150	8–50	–	500	–		
Reverse roll	0.15–0.4	–	–	–	–		
	≤40	–	–	–	–		
	≤20	–	–	–	–		
Rotogravure	0.075–0.1	–	–	–	2–5	For PSA	Lc, R
	≥0.015	–	–	–	–	change	PF, T
	15–50	–	–	1,000	–	cylinder	
	5 HMPSA	–	–	–	–	Change required	
Slot-die	120	10–85	1.5	–	–	Difficult PSA	
	0.1–10	–	–	–	–	change;	
	0.05–120	0.02−300	–	900	–	difficult web	
	*10	≤10	–	700	–	width change change	
	500	8–200	–	1,000	–		
	400	7–200	–	–	–		
MGID	≤10	20–200 ACUV	0.5	700	–		
GID	–	20–900	–	–	–		
Curtain	≤10	2–100	–	500	–		L
Kiss coat	30	–	–	–	–		
Air knife	0.1–0.3	2–3	–	–	–		
Screen	–	1–20	–	100	–		L

Note: GID, gear in die; MGID, multiple gear pumps; L, label; Lc, lacquering; PF, protection film; R, release; T, tape; ACUV, UV-cured acrylic PSA.

Roll Coaters Generally, the web to be coated is moved by cylinders built into the coating machine or the coating device, and the adhesive to be coated on the web is transferred from a van to the web and metered using a static or dynamic rod-like or cylinder-like device (i.e., a knife (blade, bar) or a metering roll).

The most simple construction, the blade coater or knife coater (knife over roll), uses a static, rod-like device to control layer thickness. Knife and blade coaters were described by Benedek in Ref. [13]. Such devices use PSAs with at least 50% solids content to deposit thick layers. Knife over roll works with an adhesive with a viscosity of 4–8 Pa · s and produces a foam level of 10–30%. The main coating device used for water-based PSAs

has been one-roll reverse coating with metering bars. This is a low-price, easily operated, flexible device. Its main disadvantage appears at high speeds where foaming may be a problem; its maximum working speed is about 200 m/min. The method is sensitive to web thickness and cylinder tolerances. The following types of knife are possible: floating knife, roller knife, and rubber-blanketed knife; smooth, wire-wound, and machined knifes are also used. Various constructions are employed for holding the knife [13]. The coated film thickness depends on the pressure before and after the blade. A knife coater is suggested for the coating of the photopolymerizable acrylic prepolymer filled with glass microbubbles and used as a transfer tape.

The Meyer rod is a wire-wound rod used in the so-called rod coating or wire-wound rod coating for metering [1]. Such a rod-coating device can use a polished cylinder to transfer the adhesive. Metering rods may be smooth, wire wound, or machined. The thickness of the coating is governed by the cross-sectional areas of the gravures between the wire coils of the rod. Adhesives for a Meyer rod coating should have a viscosity of 300–800 mPa · s (for instance, a maximum viscosity of 400 mPa · s is suggested for a 6-mm rod diameter and 0.075–0.75 mm wire), and foam generation is less than 10–20%. Such a coating device gives a coating weight of 2–50 g/m^2, with a tolerance of 15–20%. Web speed (maximum 150 m/min) and web tension influence the coating weight. The dependence of the coating weight on the rod size is illustrated by Benedek in Ref. [13]. Adjustment of the rod-coating device and of the web to be coated (e.g., wrap angle, dry edge control) are described as well. The Meyer rod can also be used for solvent-based siliconizing of a glassine paper. A coating device with a stationary roll is a variance of the rod coater [13].

In a manner different from scraper (blade, knife, rod, bar) systems, "pure" roll application (rotating cylinder) or slot-die coating devices do not use an excess of adhesive. In the case of engraved rotating cylinders, the fine (gravure) surface structure of the roll regulates the coating weight. In the case of a slot-die, the opening of the slot-die determines the coating weight. Subsequent development of both systems led to more complex metering devices. The use of several frictional cylinders or a knife on the cylinder (or round knife on a roll) allows fine adjustment of the coating weight. Roll-coating systems allow lower coating weight tolerances of about 1 g/m^2 for a broad range of coating weights (20–100 g/m^2) and running speeds (60–350 m/min).

As described in Ref. [1], roll-coating systems can work with direct or indirect mass transfer onto the web. For instance, direct gravure, direct gravure with reverse roll, and offset gravure were developed. Generally, roll-coating systems are suggested for frequent product changes and short production runs. The applicator cylinder may be polished or engraved. Principally, for roll coating various parameters exist that allow the regulation of the coating weight and coating image [4]. For indirect roll coating (using an offset roll between the metering roll and the web), the coating weight is a function of the clearance between the rolls, the cylinder speed and web speed, and the adhesive film transfer from the coating cylinder to the web. Film transfer to the web depends on the cylinder and adhesive characteristics. Adhesive transfer can be achieved by means of a rubber impression roll or gravure roll. A metal cylinder can be engraved or etched and thus its cells allow the dosage of the adhesive (gravure cylinder). Excess adhesive can be removed by a doctor blade. By introducing a transfer roll between the gravure cylinder and the pressure roll, the maximum solids content that can be coated can be increased.

By gravure coating (which is a variance of roll coating), the dosage of the adhesive is ensured by the cells of an engraved cylinder. The lay down for such a cylinder is specified for a given line number and depth. Rotogravure is also a special case of roll coating. An adhesive for rotogravure has a viscosity of 75–100 mPa · s and foaming of 2–5%. Generally, gravure coating is used for laminating (of solvent-based, solventless, and water-based adhesives) and for coating of solvent-based, water-based, or hot-melt PSAs. Direct gravure, direct gravure with reverse roll, and offset gravure were developed. Reverse-roll coaters are suggested up to a viscosity of 40 Pa · s if the mechanical stability of the dispersion is sufficient. There are two basic offset gravure configurations (i.e., with vertical and angular orientation (of the cylinders). Three-roll reverse pan-fed gravure and three-roll reverse nip-fed gravure were developed [13]. The advantages and disadvantages of various gravure systems and the control parameters of the coating weight (line number, cell depth, cell angle, solids content, and running speed) are discussed in Ref. [13]. Developments in gravure coating, which include pressurized gravure heads with doctor blade seals and coating air separation, substantially reduce air entrapment and foaming. Gravure coating is suggested for certain special products. For instance, film-based application tapes must be conformable, but removable as well. Therefore, for such products gravure printing is favored as the manufacturing (coating) method. The pattern-like, striped surface structure of the adhesive (obtained by gravure printing) provides less contact surface and better removability. The decrease of the contact surface influences the build-up of static electricity. Such a coating can be unwound with less build-up of static charges. Mixed systems, that is, reverse gravure with a closed chamber and doctor blade, are used as well.

Aqueous, cross-linked adhesives for protective films can be coated using a gravure cylinder (quad system) with 65, 96, and 120 quad sect/in. For instance, 65 quads/in. yield a coating weight of 8 g/m^2 and 120 quads/in. yield a coating weight of 4.4 g/m^2. In this case, a doctor blade provides smoothing of the adhesive surface. An intermediate cylinder and a pressure cylinder are used also.

A gravure roll with 150 lines/in. with a rubber transfer roll is recommended for silicone coating of about 0.3 lb/ream. Solventless silicones are coated using a six-cylinder coating head with an exactity of 0.7 g/m^2. In this case, a four-cylinder gravure coating has been proposed too. In both cases a coating weight of about 0.5 g/m^2 has been coated.

Heated coating cylinders with 20 lines/cm and half-moon-shape cells of 80–100 μm depth are suggested for HMPSA for a coating weight of 12 g/m^2 and 18 to 34 lines, respectively, and 40–50 μm for a coating weight of 7–8 g/m^2. The temperature of the gravure cylinder should be kept 10–15°C higher than the molten hot-melt adhesive.

Gravure systems reveal the problem that the gravure cylinder is not filled with the adhesive because of its viscosity, rheology, speed, foam, etc. There are technical solutions to avoid this problem. For instance, the accugravure system uses high pressure to fill it and the variocoater presses the knife on the cylinder to allow better filling. The so-called anilox cylinders are a special type of engraved rolls. Developments in their construction and use are described by Brinkmann in Ref. [25]. The engraving specification must be adjusted on the transfer system and include the pressure chamber-rotogravure pressure-free chamber, transfer method, normal run–reverse run direct–indirect substrates,

various coating applications, and machine speeds of 20–1,000 m/min. The history of conventional engravings includes the development from gravure cells with sharp pyramid form, insufficient release, and high danger of getting dirty to a dull pyramid with high volume and the best release. By trihelical engraving the wall area is reduced by about 30%. Laser-engraved trihelical configurations on ceramic cylinders give the best results. For the engraving of cylinders for coating (nonprinting) applications, the existing laser technology was not adequate until 2001. In 2002, laser gravure was improved, and now *U*-shape geometry is possible. *U*-shape geometry is used for siliconizing and primer coating. Trihelical engravings with up to 300 L/cm are possible and suitable for nearly all coatings. They have a very high lifetime and no problems with web-width changes. Unfortunately, this type of gravure cylinder is cleaning intensive and gives less reproducibility and volume measurement is not possible. *Cerat,* a chrome oxide-based ceramic, was developed as a printing surface material. It is very hard, but brittle.

Foaming may appear during formulation and coating. Foaming during coating depends on the volume of the recirculated dispersion. For modern machines this volume is less than 20% (e.g., for a 2,000-mm-wide web it is less than 50 l). Different coating devices require different viscosities and foaming characteristics of water-based PSAs. For instance, rotogravure needs viscosity values of 75–100 mPa · s; a Meyer rod requires 300–800 mPa · s, and knife over roll needs a viscosity of 4,000–8,000 mPa · s. The foam generation should be the lowest for rotogravure (2.5%) and it may be the highest for knife over roll (10–30%) [4]. Medium foaming is obtained for the Meyer rod.

Generally, roll coating is suggested below 100,000 mPa · s. Reverse roll coating is a special case of roll coating and is suggested up to 20,000 mPa · s. Reverse gravure is a special case of rotogravure using reverse roll. The choice of a smooth or engraved roll for reverse roll coating depends on the viscosity of the PSA. For instance, for solvent-based PSAs with low viscosity (14–15 s, DIN cup No. 4), smooth reverse rolls are recommended; for the same adhesives with a higher viscosity (20 s), gravure rolls are suggested. Gravure and reverse gravure require low viscosities. A gravure cylinder can be used for high solids (50–80%) solvent-based adhesives in the viscosity range of 15–50.000 mPa · s. Such coaters are well suited for water-based PSAs. In Ref. [4] the viscosity of common, water-based PSAs is listed. Values between 130 and 9,000 mPa · s were measured. The correlation between solids content and viscosity of dispersions includes the particle size and particle size distribution. Coatability of water-based dispersions is a function of wetting out and viscosity; wetting out depends on surface tension and viscosity is affected by diluting ability [4] (see also Chapter 8).

Reverse gravure ensures narrow tolerances for the coating weight. On the other hand, for such a coating device it is necessary to change the coating cylinder for changing coating weight. Another disadvantage is that at high speeds air may be entrained with the cylinder; that is, foaming appears. By using a closed-supply chamber, air entrainment may be avoided.

For roll coating of low-viscosity solvent-based PSAs, a pan-fed transfer coating with rotary doctor blade is suggested; for solvent-based PSAs with high viscosity, a nip-fed direct coating with metering roll and knife is suggested [13]. Coating devices for water-based systems include reverse roll, gravure with direct adhesive transfer, knife over roll, and reverse gravure. Various reverse roll coating methods are described by Benedek in

Ref. [13]. The performance of the reverse gravure coater for water-based PSAs is illustrated by the control of the coating weight (decrease from 36 to 4 g/m^2 and increase the line number from 10 to 80). The dependence of the formulation on the coater configuration is discussed also. Werner [23] describes roll coating with a machine with three or four cylinders, a web width of 600–2,100 mm, running speed up to 400 m/min, viscosity 200–150,000 mPa · s, a minimum coating weight of 16 g/m^2, and a maximum coating weight of 100 g/m^2. Roll coating with forced nip feed (*Aufsatzkasten*) with web width of 400 mm, running speed up to 500 m/min, and viscosity of 1,000–150,000 mPa · s allows a minimum coating weight of 8 g/m^2 and maximum coating weight of 50 g/m^2.

Common application systems for hot melts include rotogravure, transfer gravure, and smooth roll. Roll-coating systems for hot melts are adequate up to viscosities of 15,000 mPa · s only. For such viscosities a three-cylinder roll-coating system is suggested. Gravure cylinders are suggested for hot-melt coating for viscosities of less than 5,000 mPa · s. For lower viscosities (<70 P), a central driving system is applied and for viscosities over 50 P a forced feed of the hot-melt on the gravure cylinder is recommended. Roll-coating systems for HMPSA are suggested for a coating weight of 100–1,500 g/m^2.

For a high-viscosity, cross-linked adhesive, gravure coating may lead to a discontinuous or profiled coating layer. Such pattern coating is preferred for certain removable products (e.g., application tapes; see *Applications of Pressure-Sensitive Products*, Chapter 8). The common reverse-gravure system does not allow pattern coating; therefore, special coating devices have been developed for coating discrete portions. In special pattern reverse-gravure coating, a tampon cylinder (which contacts the gravure roll) is profiled. Such a cylinder is used for pattern coating of hot melts; dots in excess of 24,000/in.^{2} are coated with a speed of 170 m/min and specific zone-coat patterns, such as squares, circles, rectangles, or stripes, can be applied. Pattern transfer and lay down are affected by cylinder mesh size, adhesive viscosity, doctor-blade pressure and tangent point, temperature, and operating speed. Pattern coating can be applied using a perforated cylinder [13]. The combination of pattern coating with UV-cross-linkable adhesive enables zones with different adhesion cohesion properties [26,27].

Slot-Die Coaters In a different manner of knife coating, where the roll-knife distance is the main parameter to regulate the adhesive layer thickness, die systems control adhesive geometry by using an interstice-like extruder. In a similar manner to extruders, the forced adhesive transfer to the die can be ensured by a gear. The combination of a slot-die with a pump (gear with die) ensures a finer regulation of coating weight. Such a slot-orifice-die has a liquid pumping section built into the die. In this way, higher solids, higher accuracy, no foaming, and low shear are obtained. Researchers have tried to combine the forced adhesive feed of gear in die systems with the web transport/adhesive coating of roll-based systems. In the case of the slot-die, the duplex coater (i.e., slot-die and roll) uses an intermediate cylinder that transfers the adhesive from the slot-die to the web.

Generally, highly viscous melts with a viscosity up to 400 Pa · s can be coated by slot-die and coating weights of 7–200 g/m^2 are obtained. The introduction of offsetting rolls between the die or application cylinder and the substrate (see above) is a useful

technique to lower the coating weight. In slot-die the shear rate is lower than in roll coaters; thus, dispersions that need a high shear rate to be coated are not adequate for slot-die coating. The most prepolymer-based acrylic HMPSAs belong to the lowest viscosity range and can be coated with die systems. With such systems coating weights of 20–200 g/m^2 acrylic HMPSA are applicable.

An attempt to replace empirical considerations in the design of (slot-die) coating devices with engineering calculations was made by Hobbie [28]. He noted that the *Re* number of 0.001–0.01 is typical for HM coating processes, and in this range the flow is laminar. However, shear thinning and temperature strongly influence the rheology of molten adhesive. He noted that the lowest temperature dependence of viscosity (and, thus, the highest stability of the machine parameters) can be found in the temperature range 110–120°C. Because deviations in viscosity have a significant influence on the cross-profile of the coated PSA, this temperature is preferable as a working window. A pilot machine for coating of UV-curable acrylics with a maximum web speed of 700 m/min is described. For optimum mass supply, multiple gear pumps are used, which allow coating weights as low as 10 g/m^2. For transparent film laminates 2,100 working width, 15–20 g/m^2, and 250 m/min running speed are achieved. UV curing requires energy between 250 and 260 nm. The specific energy input in this range of wavelength amounts to 6–20 mJ/g/m^2 for a coating weight of 18 g/m^2.

Simple slot-dies may have coating tolerances of $\pm$1.5 g/m^2. Gear-in-die coating devices designed especially for common hot melts and highly viscous materials can coat 20–900 g/m^2. Slot-die is recommended for labels, plaster, pressure-sensitive foams, and pressure-sensitive textile materials. Slot-die is adequate for one-product, high-speed, 24-h operation if possible. Slot-die coating devices may run faster (exceeding 400 m/min) than roll-coating systems, have broader working width (3000 mm or more), produce less oxidation of the PSA, and coat more exactly ($\pm$0.5%) PSAs with viscosities up to 1 million mPa · s. The main advantages of slot-die coating for HMPSAs are that it can be used for processing of high-viscosity HMPSA; the coating device is simply constructed; the coating weight is easy regulated; and the melting system is closed, with low oxidation. The main disadvantages are that changes in coating material, coating width, start-up, and cleaning are more complex. Some formulations are not mutually compatible [4]. Cleaning is determinant for HMPSA die coating, and it depends on the die construction. The slot-die system can be cleaned only by changing the formulation and problems are caused by dirt. The abrasion of the coating device depends mainly on the running speed.

Coating of HMPSAs was described in detail by Benedek in Ref. [13]. The viscosity is the main parameter in the choice of a coating device for HMPSAs. In past decades the viscosity of hot melts decreased from 25,000 mPa · s (at 160°C) to 8,000 mPa · s. In Ref. [4] coating viscosities of common HMPSA formulations are listed. Roll coating and slot -die coating are examined comparatively; the choice of hot-melt coating cylinder as a function of the coating weight, line number, temperature, and cell depth and the gear-in-die coater (direct and offset) are discussed in detail. The dependence of coater choice on the basic formulation was investigated also. Coating defects (e.g., foaming, wetting problems, bubbles, migration, soft dry adhesive layer, legging, troubled adhesive layer image) and methods to avoid them were described [13].

According to Werner [23], a slot-die coating device with a web width of 600–3,000 mm and web speed up to 1,000 m/min can coat a PSA with viscosity up to 500,000 mPa · s with a minimum coating weight of 8–10 g/m^2 and a maximum coating weight of 200 g/m^2. Web-coating and laminating equipment with a slot-die, adequate for HMPSA, solvent-based PSA, and UV-curable compositions, is presented by Arnaboldi [29]. This machine operates at room temperature up to 240°C, with a viscosity of 50–120,000 mPa · s, and allows full coating as well as the manufacture of breathable and multiline materials. The coating weight range includes 0.02 to 300 g/m^2, with a running speed of 900 m/min. The line ensures automatic pattern changing and coating width variation without stopping the line.

Screen Printing Screen printing is a special procedure that can be applied for adhesive coating and ink printing and presents the following advantages for PSA coating: the contour (shape) of the adhesive layer can be exactly controlled, even for complex design, various face stock materials like metals, glass, and plastics can be used, there are no adhesive losses, and the coating weight can be exactly controlled within a range of 7–60 μm. Screen printing is adequate for label, tape, or protective film production. For screen printing, mainly solvent-based or water-based adhesives are used. Acrylics or rubber–resin PSA formulations have been introduced. At the beginning of the development of this technology (in the 1970s), slightly adhesive PSAs were used. Hot melts for tapes can be coated using a porous coating cylinder and a knife, forcing the adhesive through the cylinder, like screen printing (the rotary-screen printer is a hollow perforated applicator-roll) by so-called rotation extrusion. Rotary-screen hot-melt applicators for zone and pattern coating are available also. Such devices can coat double-side material. Rotary-screen printing can be used with a coating weight of 1–20 g/m^2, a running speed of 10–100 m/min, screen geometry 15–40 holes/cm, blade 1.5–30 mm; blade thickness of 150–300 μm, and pressure of 2–6 N/mm.

Solventless and high-solids silicone PSAs applicable by screen or stencil printing techniques afford a wider compositional range but require investment in screen-printing equipment. The benefits can go beyond solvent reduction to cost reduction, which could be achieved by eliminating a processing step through the direct application of the liquid silicone to a finished good rather than via a prefabricated tape. Modification with thixotropic agents may also allow better placement control during electronic part fabrication [30,31]. The thixotropic behavior allows for a balance between relatively low viscosity under high shear conditions when pumping the adhesive versus relatively high viscosity under low shear conditions after screen printing. The latter controls the slump profile, resulting in preservation of the screen or stencil print pattern.

Contactless Coating Devices In contactless coating devices the mechanical device that regulates the thickness of the adhesive layer can be replaced by air [13]. An air knife uses an air jet, which comes almost horizontally, with a pressure of 6.9×10^{-3} N/mm^2. The coating weight is regulated by the air pressure. Air-knife coating devices need a viscosity of 100–300 mPa · s and solids content of about 30% (w/w). The actual coating weight range covers 20–25 g/m^2, that is, 2–3 g/m^2 dry. In kiss-roll coating the adhesive is coated with a reverse smooth roll and the excess of latex is eliminated with an air knife. The kiss

coat is used up to 30 Pa · s. In curtain coating a continuous stream of liquefied coating falls onto the moving material. Curtain coating uses a web width of 600–3,000 mm, running speed up to 500 m/min, viscosity lower than 10 Pa · s; and minimum coating weight of 2 g/m^2 and maximum coating weight of 100 g/m^2 [23].

Spray-coating technology for hot melts has been developed from first-generation melt blown to systems with controlled fiberization. Spray coating deposits an atomized stream of material. In this case, the adhesive and air are premixed in the nozzle. Another coating process possesses a head that combines elements of both slot coating and spray technology. The adhesive is distributed to the desired pattern width through internal slot channeling. As the adhesive is extruded from the slot nozzle, heated air impinges on the adhesive from both sides, stretching the adhesive and breaking it into very fine fibers. Their main functional criteria are fiber size, fiber density, absorbency control, edge control, product aesthetics, minimal operator involvement, and air consumption. As substrates are bonded by thousands of points of contact, fiberization allows the manufacture of products with light weight and can be applied for thermally sensitive carrier materials. Coating weights as low as 2 g/m^2 can be achieved. Spray coating of hot-melts allows less adhesive consumption (up to 50%) and a discontinuous adhesive layer. For instance, for PUR foam alone used for medical tapes the adhesive is sprayed, achieving a 25–75% adhesive-free backside.

It should be mentioned that contactless coating and laminating is a general trend that includes contactless coating methods (see above), contactless printing (see Section 10.2.2.1.1), and contactless labeling (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Auxiliary Equipment The major components of a typical coating line have been discussed above, but a number of key smaller components also contribute to good running of the machine. Auxiliary equipment serves for web lamination, handling, coating, drying and curing, and moisturizing and includes winding equipment and web-control equipment. Different special equipment ensures the web-like processing of PSPs. Winding and printing devices are the most important special parts of PSP manufacturing equipment.

Winders are constituents of web-handling equipment in paper, film, and metal processing industries. Unwinder web-tension control is a main parameter. The coating and lamination quality are strongly affected by the winding, coating, lamination, web control, unwinding, and machine control [23]. Winding tension is a control parameter for (tackified) self-adhesive films (SAFs) also (see *Applications of Pressure-Sensitive Products*, Chapter 7), where the winding tension influences the pressure in the roll and the diffusion (migration) of viscous components in the carrier for SAF. Winding tension depends on the hardness of the film and must be adjusted on the winder. The fine control of the web tension was first required by the coating of soft PVC films and developed later for thin protective films. In this case, a two-component regulating system is used. The first component regulates the torque, and the second acts as feedback. Unwind reel diameter is controlled, and torque is regulated proportionally. A sensitive dancer roll measures the tension. For common films the lowest web tension is generally about 20 N, and it should not exceed 10 N for thin plastic films. Common winding machines used for blown-film manufacture

do not fulfill such requirements (because of the excentricity of the roll); here, forces of 200–300 N may appear. A surface/center rewinder allows the production of hard or soft rolls with laminates up to 200 g/m^2. Winding machines with a web-tension regulation of 50–200 g/mm^2 and web tensions of 0.1 to 10 kN are common. For blown films, the maximum winding speed is situated at 20–140 m/min; for cast films the speed is 120–400 m/min and for biaxially oriented films, it is 280–350 m/min. Horizontal surface winders are relative inexpensive, but have limitations on the width of the rolls that can be wound on small-diameter paper cores. Multidrum surface winders have been developed to allow winding large-diameter, wide rolls on small-diameter cores. Although more expensive, they allow each roll to be slit in line and shipped directly to the customer without rewinding.

Many versions of unwinders and rewinders are known: simplex, duplex, nonstop, fully automatic, with disc brakes or with DC motors, with different methods of reel-core chucking and locking, and with constant or variable tension. Flying-splice unwind/rewind stands with electronic tension control units situated between the unwind-reel stand and the first-coating-station, and the last-coating-station and the rewind stand are used. Tension can be controlled by fully regenerative DC-motor-driven draw rolls operating through a low-friction dancer roll with potentiometer and tachometer feedback reference. Tape winders are described in Ref. [23]. According to Werner [23], the main splice options are standard splice with free lap, butt splice, and butt splice with a second cover tape. In Ref. [23], a butt splicer is presented.

Special systems and machines are used for web control during and after printing and to discover and identify printing defects, image color shift, lack of labels, and splicing. Such equipment has a resolution of 0.3 mm and runs at 60 m/min [32].

Printing is a complex industry in itself. It is not the aim of this book to discuss in detail the problems related to the build-up and use of such equipment. Therefore, only some special features will be mentioned. The majority of PSPs are printed in-line during manufacturing. Such printing can be carried out on one side or both sides, in different qualities. Printing during manufacturing of a pressure-sensitive laminate may provide a technical aid for postcoating (e.g., labels; see later) or post-processing of the PSP (e.g., protective films) or serves as publicity. Solvent-based or water-based printing techniques are used. Printing with water-based inks is more difficult because of the different nature of the carrier liquid and the ink formulation components. For labels, both printing and overprinting (see narrow web printing) are carried out.

Electrostatic control is fundamental for safe conversion. This phenomenon is associated with low relative humidity also. Therefore, humidifiers (humidification systems) are used [13]. For paper processing, a temperature of 20–22°C and 55–60% relative humidity are suggested. On the other hand, excess moisture in the carrier paper can be troublesome, and it is preferred that the papers have a moisture content per weight of about 4% or less. Predrying should be employed if necessary. The use of near-infrared (NIR) spectroscopy for web humidity control is described in Ref. [33].

Static electricity during web processing accumulates and can achieve a level of 40,000 V. From a technological point of view, a reduction in triboelectricity is achieved, avoiding the separation operations during web transport and processing. Rotary machine parts,

forced web transport, and use of ionizing bars are the suggested methods. Passive and active charge-eliminating devices have been developed as well. Deionizing bars or systems (static eliminator bars that neutralize the charge with a vacuum hood to remove contaminating particles) are recommended. Ion "spray" bars used to eliminate static electricity during conversion of web-like products work with a tension of 4.5–8 kV.

Web surface, dimensions, and geometry should be controlled for uncoated as well as coated web, especially by in-line manufacture of the film carrier and its coating. Web surface control may be realized optoelectronically. Defects of 20–500 μm can be detected with a speed of 1,000 m/min [34]. Coating defects, dirt, and breakthrough can be visualised using a video zoom camera. Surface control includes gel evaluation. Gel is composed of small particles of material that did not melt completely during the extrusion process, forming the so-called gel. They are hard particles that can affect the surface to be protected by protective films. Gel content is evaluated according to its dimensions and number. As an example, for cast polypropylene (CPP) small gel particles possess a diameter of 0.02–0.03 mm^2/m^2 and big particles have a diameter of 0.1–0.2 mm^2/m. Gels can be nonpolymeric and polymeric. Polymeric gels are high-molecular-weight and cross-linked polymer molecules. Nonpolymeric gels can come from wearing screws and barrels, contamination, or undispersed pigments or antiblock additives.

Web-cleaning devices use electrically charged air jets and vacuums. Deionization with pressurized air works in 1 s up to a distance of 800 mm [35].

On-line thickness measurement is carried out with contactless sensors. According to Wiesner [36], the most used concepts for on-line coating weight determination on a web are basis weight difference dry (first measurement after unwind, second measurement after dryer); basis weight difference wet (first measurement after unwind, second measurement after coater but before dryer), and NIR back scatter (direct measurement of wet coating by detecting the solvent). NIR is sensitive to thickness differences in the substrate and chemistry, and it is used mostly for films [37]. A low-energy x-ray scanner, with a low energy gauge (thus, license free in many countries) can be used for measuring the thickness of materials with up to 15,000 g/m^2 [38]. Magnetically inductive devices work between 0.1 and 6 mm [39]. A new method combines β-weight differential and NIR back-scattering technology for on-line coating weight measurement. The procedure based on β-radiation uses the krypton 85 isotope (usable for a coating weight of 10–1,200 g/m^2), Strontium 90 isotope (usable for 200–5,000 g/m^2), and promethium 147 isotope (usable for 85–140 g/m^2).

Side control by ultrasons is possible using running speeds as high as 1,200 m/min. On-line and off-line humidity control is described in Refs [40–42].

For radiation-cured formulations the coating machine includes the curing station. The UV lamps applied in the curing channel either use electrodes or are microwave powered. Advanced cold mirror allows a reduction of IR radiation up to 80% and a decrease of substrate temperature up to 65% for film coating [43]. The advantage of excimer laser is a tailored UV spectrum. For the manufacture of radiation-cured acrylic PSAs, a UV-A band with 415–400 nm wavelength is used. Shorter wavelength deteriorates the polymer, like sunlight. The usable UV-spectrum depends on the chemical composition of the formulation. UV-A radiation is suggested for recipes in which the photoinitiator is

attached to polymer backbone; UV-B radiation (with a wavelength of 280–315 nm) is used for acrylics with an external photoinitiator. The level of curing energy depends on the chemical composition and thickness of the adhesive layer. For instance, according to Ref. [44], for a coating weight of 1,000 g/m^2 for carrier-free tape, high UV doses (e.g., 6–10 UV lamps with an output of 200–300 m watt/cm each) are used at a running speed of 2–10 m/min. A comparison of N_2 and CO_2 inertization in UV printing and finishing is given in Ref. [43]. EB curing must operate in a sealed, pressurized chamber using nitrogen or carbon dioxide. Industrial curing methods for labels (e.g., infrared, UV, EB) are discussed in Ref. [45].

10.2.2.2 Manufacture of Pressure-Sensitive Products by Other Methods

The manufacture of PSPs by other methods includes manufacture by extrusion and calendering as the main procedures.

10.2.2.2.1 Manufacture of Pressure-Sensitive Products by Extrusion

The manufacture of PSPs by adhesive coating to ensure pressure sensitivity of the web is a special case of the manufacture of PSPs. Generally, the adhesive and end-use characteristics of PSPs can be given by both the adhesive and the carrier material. The development of macromolecular chemistry allowed the synthesis of rubber-like or plastomer-like products that can be processed as film and (under well-defined conditions) exhibit self adhesivity and pressure sensitivity. Such products are made (like common plastic films) by extrusion.

It should be mentioned that the manufacture and application of such self-adhesive products are possible through the use of special application conditions, which may include elevated temperature and pressure (see also *Applications of Pressure-Sensitive Products,* Chapter 7). Generally, for PSPs with balanced adhesive properties (see Chapter 8) peel build-up is controlled mainly by dwell time. For special, low-tack self-adhesive films made by extrusion, peel build-up is also regulated by the application temperature and pressure.

It should be noted that incorporation of various ingredients in a plastic film to increase or decrease their adhesion is a general method. For instance, the extrusion technology for the manufacture of a release liner can use compounding of silicone derivatives with the plastic carrier material. Thus, release agents that do not migrate in the PSA were prepared. For instance, polyethylene (PE) mixed with the reaction product of methyl siloxane and α-diolefins, with a layer thickness of 15 μm, gives adhesion values to PSA tape of 50, 90, and 110 g/25 mm at peel rates of 0.3, 3, and 20 m/min and the adhesion retention of the tape of 98.3%.

Various classic products are manufactured by extrusion, but the main application field for this manufacturing procedure is given by self-adhesive film (see *Applications of Pressure-Sensitive Products*, Chapter 7). For high coating weights the high-viscosity acrylic HMPSAs are coated using an extruder. Sealant tapes are made by extrusion on a release film. Polyvinyl ethers (PVEs) can be coated by extrusion also. Insulating tapes for gas and oil pipe lines (see also *Applications of Pressure-Sensitive Products*, Chapter 4) are manufactured by coextrusion of butyl rubber and a PE carrier.

10.2.2.2.2 Manufacture of Pressure-Sensitive Products by Calendering

Through the use of solvent-based adhesives, a reduction in solvent content can be achieved by high-solids or by roll-press calendering (roll-press coating, press rolling) (see also Section 10.1.1.2). The use of calendering (mastication) for molecular weight regulation was discussed in Section 10.1.1.1.1. In some cases, mastication helps to realize a fully solventless mixing and coating technology. In this technology the adhesive is calendered on a continuous carrier material or a porous one. Such "press rolling" technology ensures solventless formulation of the PSA and solventless manufacture of the PSP (no need for drying, no migration, and no skin irritation), which is preferred for medical tapes. PVE is recommended for medical tapes alone or with polybutene, with titan dioxide as a filler (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Such compounds are coated warm (like a transfer mass without solvent) on the carrier web. Thus, a porous adhesive is achieved by cooling. (A porous adhesive can also be manufactured by making a latex foam.) Cold pressing and roll-press coating of (temperature-softened) masticated NR-based formulations are used for other special tapes also.

Impregnation can be used for carrier treatment and for finished tape manufacture. In this process, the coating permeates the fibers or the spaces between the fibers. In the saturation procedure, the impregnation level reaches the point where the fibers cannot hold any more liquid or the spaces between the fibers are completely filled. In the dip process, impregnation and saturation machines apply a simultaneous coating. Impregnation or saturation can be used to achieve removability (see also Chapter 8), dosage of a liquid component (see *Applications of Pressure-Sensitive Products*, Chapter 4), or reinforcement of an adhesive or a carrier material.

Prepolymer-based acrylic adhesives belonging to the medium-viscosity range have higher molecular weight and demand lower coating temperatures and shear stresses. In this case, a hybrid coater composed of a roll coater and calender coater (with two heated-rolls) is used, which ensures coating weights of 20–100 g/m^2.

It should be noted that other special manufacturing methods for PSPs are known. For instance, special adhesive compositions can be dry and cold sprayed; the PSA can also be coated as a powder. PSAs can be manufactured as powders as well. In this case, a dry blend of elastomer and tackifier is obtained as a powder that can be coated and then sintered by heating of the adherend surface. For instance, an ABA thermoplastic elastomer with a softening temperature higher than about 23°C is cooled below −20°C and pulverized; then a tackifier resin with a softening point of about 85°C is pulverized too. Thus, a dry blend of elastomer and tackifier is prepared. This powder can be dry coated and sintered by heating of the adherent surface to 177°C.

10.2.2.3 Web-Preprocessing Technology

The web-preprocessing technology includes operations required to ensure coating of the web. Web pretreatment and priming are the main web-preprocessing technologies. Such procedures use physical and chemical treatment, or coating, to impart chemical affinity to the web, required for wetting-out of the adhesive and its anchorage (see also Chapter 8). Surface treatment is used mainly for plastic carrier materials (but transfer-coated PSAs

can be corona treated also); priming is suggested for both plastic and paper carrier materials. Although surface treatment is carried out during carrier manufacture [1], refreshing of the surface treatment is generally needed before coating of the carrier.

10.2.2.3.1 Web Pretreatment

Bond strength and bond permanence are greatly dependent upon the type of surface that is in contact with the adhesive [14]. The main purpose of surface preparation is to ensure that adhesion develops in the joint between two substrates to the extent that the weakest link is in the adhesive itself and not at the interface with the adherent (evidently, for removable PSAs the weakest link must develop between the adhesive and the substrate). The anchorage of a coating on the carrier surface depends on its polarity and geometry [6]. Its polarity affects the antistatic characteristics (see also Chapter 8). Modification of surface polarity is of special importance for certain self-adhesive plastic films in which a functionalized surface must ensure instantaneous bonding (see *Applications of Pressure-Sensitive Products*, Chapter 4).

Coating of a carrier material supposes its affinity toward the adhesive. For polar carrier materials this affinity is given; for nonpolar carrier materials it must be realized by surface treatment or primer coating. Flame, chemical, or physical/electrical treatment of the web surface have been proposed. Bulk additives (or additives in a separate coextruded layer) can work as adhesion-improving agents (tackifiers) (see *Applications of Pressure-Sensitive Products*, Chapter 7).

Surface polarity influences adhesion of the coated layers on the carrier material. Paper, certain metals, and plastics are sufficiently polar to bond with PSAs. Other plastics, such as nonpolar polyolefins, special papers, or modified metal surfaces, do not possess the required bonding affinity. For instance, a common acrylic PSA exhibits a peel force of 4 N/cm on an untreated PE surface; on PP the peel force is only 0.45 N/cm. For adhesiveless PSPs (see *Applications of Pressure-Sensitive Products*, Chapter 7), increased surface polarity provides self-adhesion in the first phase of adhesion build-up. In the special case of cover films (see *Applications of Pressure-Sensitive Products*, Chapter 7), that is, of semi-self-adhesive films that adhere to the protected surface without pressure and without following adhesion build-up, the increased polarity of the surface provides the only adhesiveness of the product. The increase in surface polarity may have negative side effects also. Such a polarity increase improves surface tension. The unwinding noise of tapes depends on their surface tension (see Chapter 8).

Web treatment was described in detail by Benedek in Ref. [7]. The range of materials that can be physically treated is very broad. Generally, PE and PP carrier materials must be treated before use; polyethylene terephthalate (PET), PA, Zellglas, and aluminium may be treated in some cases too.

PE must be pretreated or precoated with a primer. PE carriers used for labels require 1 year of treatment stability. Sources to modify the PE surface include flame, laser, and UV radiation, as well as discharge from the electrical corona or plasma. These physical methods produce a combination of chemical and morphological modifications including cross-linking, oxidation, grafting of active/polar groups, chain scission, ablation, and roughening at the polymer surface [7].

Corona discharge is the most common method for surface treatment of carrier materials, which generates polar sites, increasing the free energy of the surface and bonding. Depolymerization, oxidation, and cross-linking of the treated surface are the main effects of such treatment. Nitrogen or halogens can also be fixed on the surface of corona-treated polyolefins. At a treatment energy of 500 J/m^2, about $2 - 3 \times 10^{14}$ CO groups are formed on the polymer surface. These functional groups may react with the postcoated layer; therefore, for instance, the anchorage of acrylates cross-linked with trifunctional polyisocyanate is improved by the reaction with the OH groups of the corona-treated surface.

Generally, corona treatment is recommended for PP, PS, low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), EVAc, EVOH, PA films, and paper. The effect of corona treatment is a function of the film nature, age, slip, and length of storage. Such effects are more pronounced for a film treated during manufacturing. The energy level needed for treating of various plastic films varies in the following order.

$$\text{OPP} > \text{PVC} >> \text{HDPE} > \text{LDPE} > \text{PS} > \text{PET} \tag{10.3}$$

In the range of PP films, the required dosage of treatment energy increases as follows.

$$\text{CPP}_h < \text{CPP}_c < \text{MOPP}_c << \text{BOPP}_c < \text{C}_a\text{PP}_c < \text{BOPP}_h \tag{10.4}$$

CPP homopolymer (CPP_h) needs less treating energy than CPP copolymer (CPP_c), mono-oriented copolymer ($MOPP_c$), bioriented copolymer ($BOPP_c$), calendered copolymer film (C_aPP_c), or BOP homopolymer ($BOPP_h$).

The main test methods of the effectiveness of the corona treatment are based on measurement of the contact angle or adhesion. The decrease in polarity given by corona surface treatment (measured as the contact angle; see also *Applications of Pressure-Sensitive Products*, Chapter 8) also depends on the film nature and age. The shelf life of corona treatment for LDPE film during storage and change of the wetting angle after plasma, chemical, and corona treatment were investigated by Benedek in Ref. [7]. The decrease in surface tension is about 3–5 mN/m after the first 2 days for an aged film and 1–3 mN/m for a "fresh" (extruded) film. There is an interdependence between the effectivity of the corona treatment, storage time, and concentration of the slip agents. The shelf life of the corona treatment for PP is longer than that of similarly treated PE. Orientation also influences the corona treatment; the corona treatment of OPP and BOPP is more difficult, requiring high dosage. The energy level needed for the corona treatment of BOPP may be 10 times as high as that needed for PE. Generally, corona treatment of PP during film manufacture (before migration of slip) yields better results. Electrically conductive printing inks make corona treatment difficult. In a different manner from plastics, corona discharge activation of elastomer surfaces leads to a new polar surface with a very short shelf life. Reconstruction of the elastomer surface may occur within minutes after treatment.

To improve the self-adhesion of (adhesiveless) polyolefin films, their functionalization and high-pressure/temperature lamination has been developed (see *Applications of Pressure-Sensitive Products*, Chapter 7). Such functionalization can be carried out by corona treatment. High-pressure/temperature lamination uses a laminating machine for film application.

Corona treatment requires working with high-voltage (10–25 kV), high-frequency (30–50 Hz), electrical fields. Values of 12–20 kV and frequencies of 1–3.8 MHz and 15–40 kHz were also tested. A higher frequency improves the corona treatment effect, whereas low frequency leads to blocking of the films. The so-called streamers (discharge channels during treatment) appear above a frequency of 10 kHz. For PP, treating energies of 0.15–40 J/cm^2 have been used. Corona power supplies possess an output of 4–60 kW. Watt density readout equates the constant treatment-level measurement. Electrode width and watt density level are programmable and adjustable via software. There is a skip treat option, which means that there are intermittent treat and nontreat areas along the web length; that is, full-surface and partial treatment are possible. Threat areas are synchronized with line speed. A splice mode option moves electrodes from the base roll to permit the splice tail to pass. Corona treatment has a special importance for adhesiveless self-adhesive films (see also *Applications of Pressure-Sensitive Products*, Chapter 7).

Advances in the fundamentals of corona treatment led to new treatment procedures such as hot-air-jet corona, indirect corona, spray corona, corona deposition, and aerosol corona.

As mentioned previously, corona treatment is hindered by the migratory additives in the films. During past years additive levels have steadily increased [7]. Now, high-slip PE contains a 2000 ppm slip agent in comparison with 800 ppm from a decade ago; therefore, treatment of such films became difficult. Slip additives can be volatilized by using a high-temperature air jet and, therefore, corona treatment can be improved by using a hot-air jet to blow up the slip agents from the film surface. Thus, better treatment-stability is achieved.

Indirect corona treatment without a counterelectrode has been developed also. With this system it is possible to treat flat materials of any thickness, and the working distance can be increased up to 20 mm. The shelf life of PP films treated by indirect corona is longer than that of films treated with direct corona discharges. Electrically inhomogeneous materials (containing metals) and contoured items can be treated with "spray corona" systems, which use a gaseous agent.

Another new method of corona treatment that prevents the fast fading of surface energy was developed in the 1970s. This process is based on the deposition of an ultrathin chemically active layer of SiO_x (made from silanes and oxidizing agents), a so-called "corona deposition." Therefore, the corona discharge is carried out in a controlled (nitrogen) atmosphere with controlled amounts of silanes and oxidizing agents. The surface tensions achieved with this procedure are higher (50–52 mN/m) than the values achieved by common corona treatment (40–43 mN/m). This procedure of corona discharge in a gas atmosphere started the development of corona discharge combined with aerosol deposition. The aerosol deposition can be carried out simultaneously with the corona discharge or after the corona treatment. After a storage time of 10 weeks, the aerosol corona-treated film (PP) has a surface tension of about 55 mN/m compared with 48 mN/m for the film treated with common corona discharge.

Flame treatment is preferred for packaging tapes and offers advantages where moisture should be driven out. The temperature of the flame is about 1200°C. Chemical and flame treatments yield better adhesion values than corona treatment.

PE for tapes must be chemically pretreated. Such chemical etching produces a hydrophilic surface and creates sites for adhesion. For PE, different chemical treatment methods have been tested. Solutions of metal salts (e.g., Zn, Ba, Al, Sn, and Mg chloride) improve the anchorage on a chemically oxidized PE surface. Most commercial etching compositions are solutions of chromic acid or chromic acid and sulfuric acid. Potassium bichromate, sodium hypochlorite, potassium permanganate, zinc chloride, and aluminum, barium, and magnesium chlorides can be used as well. For instance, PET can be chemically treated with acid–potassium bichromate mixtures (5–30 s at 75–80°C) or sodium hydroxide and acid–potassium bichromate. Recently, a new procedure based on sodium hypochlorite and acetic anhydride was developed [46].

Fluorination is a special variance of chemical treatment with gases. This method allows the treatment of complex profiles and forms [e.g., bubble packs to be coated with PSA or ethylene–propylene–diene multipolymer profiles] and of foams more than 2 mm thick (e.g., PE–VAc foam) and does not cause pinholes. It is used for manufacturing barrier layers as well. First, chlorine was applied as a gaseous reactive together with UV radiation; later, a mixture of fluorine and nitrogen was tested. Recently, the use of sulfonation (treatment with an SO_3 atmosphere) was studied. Surface treatment with fluor was examined comparatively with corona treatment in Ref. [7].

In corona treatment air contains about 100 ppm ozone. Pollution control regulations call for the elimination of ozone, and ozone-eliminating systems are required. On the other hand, ozonization is also used for surface pretreatment. In this case, the ozone concentration attains 12,500 ppm. A combined treatment with ozone and UV light has been tested as well. Surface oxidation by UV or ozone has an overall effect similar to that of certain plasma and flame treatments. Treatment with benzophenone under UV light produces cross-linking of the surface without increasing its hydrophilicity.

Plasma treatment can be used too and allows a 4- to 12-fold improvement in adhesion (depending on oxygen and ammoniac plasma treatment). Sheet-like products or rolls can be plasma treated. The advantages of the procedure are that there are no pinholes, no side effects, and no static charges and low energy is required. The charge is maintained for a longer time. Plasma treatment was examined in comparison with chemical and corona treatment in Ref. [7]. There are many variances of plasma used for treatment, for example, chemically inert plasma, reactive nonpolymerizing plasma, reactive graft-polymerization plasma, and reactive polymerization plasma.

Generally, plasma treatments are subatmospheric processes, working at low pressure (60–150 Pa), between room temperature and 250°C, at frequencies up to 2.45 GHz, but atmospheric plasma treatment was developed as well [47]. Plasma treatment can be applied as a pretreatment for better adhesion, degreasing, roughening, activating, and priming. Plasma treatment affects deeper molecular layers than corona treatment and produces cross-linking.

For improvement of the surface affinity and adhesive anchorage, chemically reactive plasma (e.g., oxygen, fluorine) can be used. If a reactive, nonpolymerization plasma treatment is applied (with fluorine, oxygen, or nitrogen), multiple effects appear. Low-molecular-weight substances from the polymer surface are eliminated, and polar groups are formed. The effect of oxygen plasma is twofold: active surface groups are generated that allow good adhesion properties and reduction of the defects yields a smoother

polymer surface. According to Dorn and Wahono [48], a PP surface with a contact angle of 90–92° with water before treatment displays contact angles of 63–85° after plasma treatment, in comparison with corona treatment, where contact angle values of 60–62° have been obtained. According to Ref. [48], PP can be plasma treated using oxidative gaseous mixtures only; PE can be plasma treated using nonoxidative gases as well. Dorn and Bischoff [49] noted that by treating PP with oxygen plasma at 1 HPa and 27.12 MHz, the same dependence of bonding strength on time was observed as that by oxidative chemical treatment with chrome–sulfuric acid.

All pretreatments induce various functional groups into the surface and cause molecular modification to varying depths. The pretreatments also modified the surface topography of the PP in some cases by roughening the surface and causing the creation of new features, such as those created by flame. Green et al. [50] noted that with a surface analysis of pretreated PP, based on functional groups and the O:C ratio (using various treatment methods such as corona, flame, fluorination, vacuum plasma, and air plasma) vacuum-plasma induced oxygen into the surface in higher concentrations and closer to the surface than nitrogen. According to Kaute and Buske [51], up to 30% oxygen has been measured after treatment compared with 10% measured after corona treatment.

The formation of double bonds, cross-linking, and redox reactions is initiated by plasma. Dorn and Bischoff [49] discussed the modification of PP tacticity also. The superficial weak boundary layer is eliminated. This effect was observed for PP, but not for PE.

Plasma treatment with graft polymerization leads to an increase of surface adhesion also. First, an inert plasma treatment is carried out and then the activated surface, which has long-living radicals, is reacted with polymerizing monomers. This procedure is really a plasma treatment, followed by coating at low temperatures to modify the polymer surface. Plasma treatment has been used to simultaneously improve the wetting characteristics of PET and reduce static charge accumulation by triboelectricity. For instance, the wetting angle with water has been reduced from 75° to 60–35° by using acrylic acid as the reagent, which is coated with a thickness of 15 to 20 Å. Unfortunately, although the electrical conductivity has also been improved by an order of magnitude, it does not fulfill the practical requirements. Plasma treatment for film is mainly a batch process [52].

Plasma-treated surfaces lose their surface treatment also. However, the treatment stability during storage is better for the plasma process in comparison with corona discharge. For instance, a loss of 15–20% of treatment effect has been found in about 1 month.

10.2.2.3.2 Web Priming

Primer coating is generally required for coextruded products with a complex build-up, but it was a need for the main polyolefin-based adhesive-coated carrier materials also. Advances in the carrier formulation, carrier treatment, and adhesive coating allow the use of primer-free web processing also, but generally, such adhesive compositions (used mainly as protection films) must be more cross-linked or they are coated with a lower coating weight.

Primers are adhesion promoters (see also Chapter 8)**.** Adhesion promoters are used to improve adhesion (anchorage) of a liquid postcoated layer (mainly an adhesive, a release layer, or a printing ink) on a solid-state carrier material. For instance, with the exception of the combination of BOPP/water-based adhesive and filament-reinforced

BOPP/hot-melt adhesive (with higher stiffness and lower contact surface), strapping, packaging, and masking tapes (see also *Applications of Pressure-Sensitive Products*, Chapter 4) need a primer. Chemical primers provide a bond between the substrate and adhesive. They are supplied as solvent-borne, water-borne, or solid-state products (see also Chapter 8). The need for primer coating influences the complexity and economics of PSP manufacture. The available equipment can influence the choice of primer and determines whether the primer is to be applied in-line or off-line. Common application systems for primers include roll coating with rotogravure, transfer gravure, and smooth roll, with coating weights of 0.01 to 0.5 g/m^2. The application and mechanism of primer coating for direct and transfer coating are described in Ref. [7]. In direct coating the primer improves the anchorage (increases the chemical affinity, no smoothening effect is required), strengthens the face stock (enforces the fiber structure, strengthens the surface layer), absorbs stresses, stiffens the face stock material (changes the peel resistance and cuttability), limits adhesive bleedthrough, and influences drying. For transfer coating the primer improves anchorage (smoothens the paper face stock, increases the chemical affinity), strengthens the face stock, absorbs stresses, and stiffens the face stock.

10.2.2.4 Web-Postprocessing Technology

Generally, web-postprocessing technology includes lamination and overcoating. For special products web-postprocessing may include finishing the adhesive. Finishing the adhesive is imposed generally for in-line adhesive manufacture using postcuring or postpolymerization (see Chapter 1). In this case, the coating machine includes as auxiliary equipment the radiation-curing devices (see *Auxiliary Equipment,* in Section 10.2.2.1.2).

Foaming (simultaneous or postcoating) has been developed for the manufacture of special tapes. Such methods are not used for common labels. The physical foaming technology of adhesives was discussed by Klein [53]. In this procedure, typical hot melts increase their volume by a factor of 2, whereas the density compared with nonfoamed materials decreases to 50%. A closed cell foam is generated with skinning on the surface. The usable viscosity range includes 1,000 to 40,000 mPa · s.

Both lamination and overcoating (e.g., printing and lacquering) are procedures used in the manufacture of PSP, such as in their conversion (see *Lamination*, in Section 10.2.2.4.1, and *Label Printing* in Section 10.3.2.1.1).

10.2.2.4.1 Lamination

Lamination is the bonding of two different layers by pressure using an adhesive or a molten polymer. Generally, laminating procedures include thermal, extrusion, and adhesive lamination (see also Figure 3.1 in Chapter 3). Lamination is required for multiweb constructions. Such constructions are PSPs with separate release liner (e.g., labels and certain tapes; see also *Applications of Pressure-Sensitive Products*, Chapter 1). The main part of lamination equipment is a nip between one rigid and one elastic cylinder, so that enough pressure is achieved to contact the two materials.

The manufacture technology of PSPs by coating and lamination is a part of classic lamination technology. In the manufacture of packaging films, web-like carrier materials are coated with adhesives to produce laminates (i.e., adhesive-bonded web or

sheet-like composites). Later, a similar coating and laminating technology was used in the production of PSPs. For instance, so-called "security foiling" (i.e., overlamination of the label with a destructible upper layer) is a common technology to manufacture security labels.

From the technologic point of view, the main and distinct characteristic of label-production machines is the existence of a laminating unit necessary to build up the label laminate from the face stock material and the separate solid-state release liner [9]. Common tapes and protective films do not need such equipment (see *Applications of Pressure-Sensitive Products*, Chapter 4).

The adhesive–lamination process is influenced by lamination technology, laminating components (e.g., adhesive, substrate), and laminating machines. Dry lamination is a procedure in which the wet adhesive is coated on a carrier material, dried, and then laminated, generally on-line with another carrier material. PSAs can be used as adhesives for dry lamination also. The criteria for choosing one or the other technique should be based on technical performance, cost, and environmental impact.

Economic considerations forced the in-line manufacture of PSPs, and for this technology production equipment for simultaneous adhesive and abhesive coating and lamination has been developed. In-line extrusion of the film carrier and its coating are possible also. The main problem is that relaxation processes in the extruded film are time dependent. Such processes may lead to changes in the geometry or surface quality of the films.

10.2.2.4.2 Web Overcoating

Overcoating of the laminated web includes its printing and lacquering. Both procedures are part of PSP manufacture and PSP conversion. However, their complexity differs according to the product class of PSPs.

Web Printing Printing is carried out for the components of the pressure-sensitive web (e.g., face stock, release liner), for the laminated web as a manufacturing step of the web-like PSP, and as a converting operation for the confectioned pressure-sensitive item (e.g., label, form). Printability of the laminate is discussed in Ref. [7].

Adhesives are coated on the carrier material with the use of special coating devices (see *Coating Equipment*, in Section 10.2.2.1.2). Other components (inks, antistatic agents, primers, etc.) are coated with common printing techniques. In some cases, the adhesive or the release agent can be coated with these printing techniques as well.

Most PSPs, such as labels or certain tapes, are information carriers. The information must be printed on them before their end use. Generally, printing occurs first during the manufacture of the web-like, nonconfectioned product. For some products (mainly labels and tapes), a postprinting of the confectioned (cut, die-cut, etc., product) can be carried out also, and in some cases printing (writing, stamping, etc.) can be done during their end use. Therefore, one can speak of printing and postprinting. Web printing affects postprinting.

Some time ago, the basic printing methods for printing a PSP during the manufacture of a web-like product and for postprinting (in the prelaminated, confectioned, or postlaminated state) were the same. Differences were given by the web width and the combination of special materials and printing/confectioning technologies. Some years

ago, special nonimpact printing methods and computerized design and printing of PSPs were developed. Thus, the last step in conversion, or printing, is transferred to the end user (or "almost" end user). Therefore, printing and postprinting technologies now (and in the future) may not be the same. As a consequence, the surface quality (printability) required for a certain printing method used in the manufacture of the web-like product (e.g., flexoprinting of a plastic film) could differ from the surface quality required by postprinting of the confectioned product (e.g., screen printing or laser printing). For printing during product manufacture (e.g., web printing for protective films or tapes), in-line presses are used, where the inking and impression cylinders are in-line with the web. Printing presses with UV-flexographic and rotary screens or digital offset printing are used. Taking into account the different complexity of preconverting printing and product printing, printing-related problems will be discussed in Section 10.3.

Web Lacquering Lacquering (varnishing) is a full-surface coating, that is, a special case of printing, and uses common coating techniques. Lacquering affects post printing.

As discussed in detail in Ref. [1], carrier manufacture for labels may include coating. In this case, web (post)lacquering is not necessary. For certain label manufacturers, the surface quality (gloss, adhesive anchorage, etc.) should be improved chemically. Therefore, the film must be coated with a lacquer; the off-line top-coated film is converted into a pressure-sensitive laminate and later processed and printed on the lacquered side as a narrow web. For instance, top-coated superwhite, opaque PP films with a thickness of 50 and 60 μm have been developed for labels. The top coating of such films can be printed by letterpress, UV silkscreen, litho, UV-flexo, and thermal-transfer printing processes. Top-coated PE and PP films display the advantage of better printability and environmental resistance. Therefore, about 15–25% of polyolefin films used in Europe as label carriers are top coated. Such films are lacquered by rotogravure. Generally, lacquering can be required to ensure printability or to improve the optical image of the product, to protect the coated carrier, or to ensure processibility. The standard pretreatments carried out by foil manufacturers are not sufficient to meet the extremely high requirements for printability in the field of computer printing. Although PVC foils can be easily printed, OPP foils may require considerable effort to satisfy special requirements. The possibilities for chemical print treatment are often limited if the result is to be highly transparent. Certain pretreatments can only be achieved with opacity. Therefore, lacquering of the face stock material is a necessity in many cases. Lacquered, synthetic carrier materials with a surface coating can be printed with the usual paper printing inks in all normal printing processes; they can be used in copiers, laser printers, and color ink jet printers.

Films with high opacity and reflectivity are required for special printed labels. High opacity ensures accurate scanning; high reflectivity given by a glossy surface offers high print contrast for bar codes, which is necessary for scanning accuracy and high first-read rates. There are a number of ways to produce a white label, based on a clear, colorless carrier material. A white pigment can be added to the adhesive, or a white top coat can be applied to the clear film. Full-surface lacquering of paper labels, followed by UV curing, improves their gloss.

A vapor-deposited aluminum layer is sensitive to mechanical stress (wear) and oxidation and must not remain unprotected on the front of the label. Therefore, it is covered with a top coat. Such a primer offers excellent conditions for standard print processes. Linerless labels are supplied as a continuous tape-like, mono-web material (see *Applications of Pressure-Sensitive Products*, Chapter 4); a special coating on the top surface of the label prevents blocking of the adhesive layer.

Lacquering (varnishing) can be done on-line or off-line, with dispersion varnishes or with EB-curable varnishes. There is a wide variety of dispersion, ink unit, oil print, functional, and NC varnishes; UV-curable and calendered varnishes can be added also. Varnishes can be applied by using water pans, varnishing units, varnishing modules, or coating units (tower). Direct or offset lacquering can be carried out. The direct procedure allows thicker varnish and ink coatings, improving the mechanical properties and gloss of the product. The ability to be lacquered is a common quality parameter for semifinished products for pressure-sensitive labels.

Lacquering by gravure printing yields the best results; three- or four-cylinder coating devices are used. Such a procedure allows coating of up to 4 g/m^2 (wet) lacquer. Lacquering is carried out by using 60-line gravure printing, to a gravure depth of 45–50 μm. For instance, the UV-cured lacquer for labels is coated with a gravure cylinder (80–120 lines/cm, 12–20 μm depth), with a coating weight of 2–4 g/m^2.

10.3 Conversion of Pressure-Sensitive Products

Conversion of PSAs was described by Benedek in Ref. [7], and conversion of PSPs was discussed in detail in Refs [13,54]. Depending on the laminate components, type of adhesive, and lamination place, adhesive-coated finished products are supplied as permanent laminates (e.g., paper, film, etc., laminates according to the carrier material use for PSPs), temporary laminates (e.g., overlaminating films, labels, special tapes), or as monowebs (tapes, protective films, etc.). For the latter products, laminating occurs during application. Thus, laminating to produce web-like materials is used for the manufacture of PSP components (e.g., carrier, release liner), for the manufacture of the finished product (e.g., label, business form), or to allow the end-use application of PSPs (labels, tapes, or protective films). In the case of labels, delamination of the liner precedes end-use lamination on the substrate. Unwinding of tapes and protective films can be considered delamination also. The influence of the formulation on the converting properties (e.g., shrinkage, lay flat, migration) and confectioning properties (slitting, cutting, diecutting, winding, etc.) was discussed in Ref. [4]. Converting properties of PSAs (e.g., lay flat, dimensional stability, surface quality, cuttability) are described by Benedek in Ref. [7] (see also *Applications of Pressure-Sensitive Products*, Chapter 8).

The use of PSPs is possible due to their adhesive and mechanical characteristics. As discussed throughout the preceding chapters, PSPs are manufactured generally as web-like products. They are applied as a web-like, or finite, discrete product whose dimensions or surface characteristics differ from those with which they were manufactured. Therefore, before application they must be finished. In this case, finishing means the transformation of the continuous, web-like product that has the optimal geometry for

manufacture in a product that has the optimal characteristics for use. This production step is called conversion. Benedek [1,54] discussed convertibility as the sum of the convertibility of the PSA and that of the pressure-sensitive laminate. Convertibility of the PSA has been described as its coatability (see also Chapter 8). Convertability of the adhesive is a function of adhesive properties and the solid-state components of the laminate on the coating technology and the end-use properties [7]. Convertability of the PSP depends on the laminate construction. The adhesive properties of PSAs are described in detail in Ref. [14]. The adhesive properties of the PSPs are discussed in Ref. [55] (see also *Applications of Pressure-Sensitive Products*, Chapter 8). The solid-state components of the laminate are described in Ref. [7]. Manufacturing of the carrier material (e.g., paper, synthetic films, foams), the performance characteristics of the main films (e.g., PE, PP, PVC, PET, PS, PA, cellulose acetate, cellulose hydrate, EVAc copolymers, PUR, polycarbonate, polyacrylate), the general requirement for their use as carrier and special requirements for their use as carrier for labels, tapes, and protective films, and their postextrusion modification and surface modification of synthetic films were discussed by Benedek in Ref. [1]. Paper and plastics were examined concerning their converting properties comparatively [7]. Laminate manufacture was described in Refs [1,13]. The influence of release liner on coating, converting, and labeling properties was examined in Ref. [7]. Laminate construction is discussed in detail in Refs [1,55]. The influence of the adhesive design and formulation on the converting properties was discussed by Benedek in Refs [4,12]. For some PSPs, coating is included in their conversion as printing or lacquering (see above). Certain PSPs are not coated (e.g., extrusion-made products; see Section 10.1.2.2). For some products, converting includes cutting (slitting), laminating or delaminating, die-cutting, and other mechanical operations (called confectioning). Other PSPs are not laminated and not cut, but torn. Numerous PSPs are used for applications in which the adhesive and mechanical performances must be complemented with other properties. Therefore, these products have certain special performances called conversion properties.

For PSPs manufactured by adhesive coating, converting properties are also influenced by the adhesive (see also Chapter 8). Although the characteristics of the solid-state components of the laminate (face stock and release liner) and the manufacture technology of the laminate influence the conversion properties, in this process the requirements of coaters and laminators primarily concern the adhesive. Certain conversion characteristics like die-cutting and stripping affect product application (see *Applications of Pressure-Sensitive Products*, Chapter 4). The adhesive must exhibit good resistance to gum balls, edge flow, and face bleed (see *Applications of Pressure-Sensitive Products*, Chapter 8). On the other hand, high-speed converting machines solicit the label material mechanically. For instance, electronic confectioning machines for labels cut, die-cut, punch, and perforate the paper with a running speed of 200 m/min. It should be taken into account that the ratio between stiffness and thickness (specific thickness) is higher for plastic films than for paper. This allows higher processing speeds.

Manufacturing lines allow preprinting, silicone release coating, adhesive coating/second web lamination, die-cutting, waste stripping, and fan folding, all in-line, in one pass [56].

10.3.1 Confectioning

Confectioning includes mechanical processing by slitting, cutting, die-cutting, perforating, and embossing. The confectioning properties of the main PSPs were described in detail by Benedek in Ref. [54]. Confectioning requires roll and sheet material handling equipment, equipment for cutting in the machine direction (slitter) and cross-direction (cutter), sheeter and surface treating apparatus, die-cutting and embossing equipment, perforating equipment, and windowing and tag machines. Confectioning machines for labels cut, die-cut, punch, and perforate the web. The dimensions of the processed materials and their characteristics can vary widely. Thin films of 15–20 μm as well as thick paper (e.g., cardboard of 300 g/m^2) can be processed.

Special preprocessing and postprocessing operations are related to printing. Thus, humidification/dehumidification, ionization/deionization, decurling, coating/varnishing, cleaning, line/hole punching, and preprinting can be carried out before printing. Varnishing, overprinting, laminating, die-cutting/waste removal, cross-perforating, slitting, and quality control should be carried out after printing.

Conversion of labels is the production of narrow rolls (or sheets) of finished labels, postprinted, die-cut, slit-cut, perforated, and rewound. A revarnishing may be necessary, requiring a separate drying unit (e.g., a UV dryer). Machine-direction cutting (slitting) or cross-direction cutting of the web are common operations for labels, tapes, and protective films. Die-cutting is generally the operation that transforms a pressure-sensitive web into a label (or business form) laminate, but it is used for special tapes also. In-line sheeter, nonimpact variable information printer, or web tinter can be attached. Electronic web-tension devices, web-guide sensors, and reinserters of preprinted web are used as auxiliary equipment. In-line sheeters allow form producers to compete by extending the cut-sheet laser and ink-jet market. Certain form-printing machines offer custom-built commercial jaw folders to produce complete printed parts. Certain security labels have a complex construction (see *Applications of Pressure-Sensitive Products*, Chapter 4). Their conversion includes a range of operations and requires special equipment.

10.3.1.1 Slitting and Cutting

Cuttability of the carrier material is required for labels during their manufacture. For tapes it is also needed during lamination. For protective films it is necessary after their application in a laminated status (e.g., laser cuttability). For all these products, cuttability is also required in the conversion step of manufacture. The general aspects of cuttability are discussed in a detailed manner by Benedek in Refs [1,7,54]. Cutting is the operation carried out to transform the full-width web into end-use width reel material by slitting or into sheet material by transverse cutting. Simultaneous cutting in both directions is required for plotter film (pattern paper) cutting. The various types of cutting include cutting through (e.g., slitting and cutting), cutting out of the top layer (die-cutting), perforation, engraving, and marking. The importance of cutting and die-cutting differs for various PSP classes. Dimensional stability and die-cutting properties of common films versus paper are discussed in Ref. [7], where the main parameters of dimensional stability of films (e.g., built-in stress–strain and chemical resistance) and shrinkage

TABLE 10.4 Main Characteristics of the Cutting Technology

Cutting during Conversion								
			Cutted Product		Cutted Laminate Components			
Full Section	Partial	Cutting Line	Reel	Sheet	Carier	PSA	Full Laminate	Finished PSP
Slitting	—	Linear	•	—	—	—	•	Narrow web (label, tape, protection film)
Guillotining	—	Linear	—	•	—	—	•	Sheet (label, protection film)
Plotter cutting	◦	Various	—	•	•	•	•	Sheet
Other (heat, laser)	◦	Various	—	•	•	•	•	Sheet
	Die-cutting	Linear	•	•	•	•	—	Sheet, reel (label)
	Other	Various	—	•	•	•	•	Sheet
Cutting after Product Application								
Guillotining	—	Linear	—	•	—	—	•	Protection film

Note: •, valid; ◦, main.

(e.g., built-in cohesion, cohesion stability, and plasticizer stability) were also examined. Flagging and its dependence on printing were discussed also (see also *Applications of Pressure-Sensitive Products*, Chapter 8). The main characteristics of cutting technology are summarized in Table 10.4.

Products supplied and used as continuous, web-like materials must be cut into narrow webs. In this case, slitting is the main cutting operation. These products include protective films and the main tapes. In-line slitters remove the edges of (trim) the material and also divide (slit) the web laterally into two or more narrow widths (ribbons) that are formed into individual rolls on the rewinder. Off-line slitters receive full-width rolls and form rolls with small diameters. Off-line slitters are normally used when the finished rolls have smaller diameters than the unwinding roll and when there are many narrow ribbons. The jumbo-size coated rolls are transferred from the rewinder to a special slitter–rewinder that produce small retail or consumer size rolls of tape. Narrow-width rolls range from 12 to 25 mm and contain 3–30 m of tape per roll. The automatic rewinder checks, counts, and cuts labels, foil, and paper. The requested number of meters or the number of labels can be chosen on display. Common slitting machines (600/800/1,000 mm width) have a changeover time of about 40 s for finished rolls.

Other products are finite elements cut out from the continuous web. In this case, cutting is carried out throughout the whole section of the web (e.g., transformation of reel material into sheet material) or through the face stock material only (die-cutting) to preserve the web-like character of the product, that is, to ensure automatic handling, conversion, and end use. New slitter, cross-cutting machines have been claimed to provide absolute flatness without curl of the extruded material. Cross-cutting is by the guillotine or pendulum method.

A dual-knife sheeter for high-speed work is a rotary dual-knife cutter with a delivery and stacking system. Metal-to-metal contact occurs between the upper and lower knives. For such machines, sheet length and square accuracy of ± 2.5 mm can be maintained continuously.

An evaluation of cuttability is described by Benedek in Refs [7,54]. Converting involves processes such as die-cutting of roll stock and guillotining of sheet stock. The main characteristics of the cutting process (slitting, guillotining, and die-cutting) and its application for various PSPs as a function of the cut material (laminate or laminate components) were described in Ref. [54]. A linear or in-plane cutting line is used. Guillotine cuttability tests have been carried out by Benedek [7]. Cuttability for various laminates was evaluated using the cuttability index. Such an index takes into account the mobility of the cut material after cutting and adhesive deposit on the cutting knife after a given number of cutting operations. Blocking and pulling up of the cut material are secondary phenomena produced by smearing of the cutting and cut surfaces. The best results were obtained with cross-linked adhesives and solvent-based adhesives in comparison to common, water-based PSAs. Acrylics possess better cuttability than formulations with CSBR dispersions. Priming improves cuttability also. The various product component-related and construction-related parameters influencing cuttability were investigated and mathematicized. The main problems of guillotine cutting (e.g., smearing, blocking, and adhesion of the cut material) were discussed. Cuttability depends on the plasticity and elasticity of the material. Both the solid-state components of the PSP and the adhesive influence cuttability. The cold flow (creep) of the adhesive is one of the main parameters of cuttability; its dependence on the rheology (viscosity and modulus) of the adhesive, chemistry, and geometrics of the adhesive was described (see also *Applications of Pressure-Sensitive Products*, Chapter 8). The interdependence of cuttability–peel resistance–shear resistance–tack was also examined. Guillotine cuttability strongly decreases with tack. Formulating modalities that improve the high-frequency modulus of the adhesive will facilitate conversion. For good cuttability, a minimum of hot-shear gradient (see also *Applications of Pressure-Sensitive Products*, Chapter 8), low peel resistance, and low tack are required. As noted, 10–30% cuttability improvement requires 80% peel decrease or 50–80% tack decrease.

The solid-state components influence cuttability as well. For instance, LLDPE is neither foldable nor stiff. It is difficult to cut or die-cut and punch because of its high elasticity. Its extensibility is a disadvantage for the converter. In this case, special cutting tools with a higher pressure should be used. There is also a trend toward multilayer films (five to nine layers); such films are more difficult to cut. Blocking after guillotine cutting of paper-based PSPs is a disadvantage given partially by the compressibility and porosity of the cut section.

The influence of the solid-state components and that of the adhesive on cuttability has been discussed in a detailed manner in Refs [7,54]. As noted, the mechanical performance characteristics (e.g., flexural resistance) and geometry of the solid-state components are decisive concerning the cuttability of pressure-sensitive laminates. Cuttability depends on the thickness of the adhesive and on the laminate thickness and stiffness (nonlinear increase) [54]. The stiffness of film labels and paper labels was examined comparatively (paper displays higher stiffness). The influence of the number of layers, build-up of layers,

adhesive nature, siliconizing, coating weight, embossing, priming, and solvents on laminate thickness and laminate stiffness was examined to correlate these parameters with cuttability. The dependence of guillotine cuttability (C_G) on the adhesive (A), face stock (F), and release liner (R) can be described by a correlation of the form

$$C_G = f(\alpha A), (\beta F), (\gamma R) \tag{10.5}$$

where the coefficients α, β, and γ possess values of about 0.15; 0.42, and 0.42; that is, the solid-state components are decisive for guillotine cuttability.

Waste-stripping properties (by labeling) of an adhesive are very important. Such characteristics depend on the adhesive properties (see later). The slitting properties of the tapes strongly depend on their rewinding ability. Rewinding ability (considered peel resistance on the carrier backside) is a function of the adhesive performance as well. However, in the case of die-cuttability, the deformability and tear characteristics of the solid-state components and the global rigidity of the laminate play a major role (see later).

A special case of cutting is the processing of plotter films. For such films, cuttability is an end-use performance characteristic. Texts and logos are cut with a speed of up to 400 mm/min. Roll and sheet cutters have been developed that not only have a cutting mode, but also can be used for drawing. Plotter cutting is very-high-speed cutting. For instance, tabletop plotter-cutting machines work with a speed of 800 mm/s and can process films with a width of 50–600 mm.

10.3.1.2 Die-Cutting

Conversion involves processes such as die-cutting of roll stock and guilottining of sheet stock. Die-cutting is partial cutting of the laminate into laminate sections; it allows the transformation of the web-like face stock material into discrete items, such as labels, which can be applied using a web-processing apparatus [54]. Die-cutting is of great importance for labels. For special medical tapes, where discontinuous constructions are used to allow breathing and diffusion, die-cutting is also important (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

For labels or label-like products, the cutting equipment is generally integrated into the converting/printing line. For instance, nameplate type printing units possess an automatic cutter (see also *Applications of Pressure-Sensitive Products*, Chapter 4). For labels operating on-line finishing equipment supposes the existence of a die-cutter and matrix stripper, rereeler, sheeter, etc.

Die-cutting requires that the label be designed and its shape and distribution of label area on the web be calculated to allow web (and waste matrix) transport/removal after die-cutting. The unusable areas surrounding the cut labels are stripped from the release paper and wound into a roll. The cut labels remain attached to the release paper and are wound into rolls also.

Flat-bed cutters, rotary cutters, and wraparound dies are recommended for labels. Die-cutting machines can be either nonrotary or rotary. Nonrotary mechanical die-cutting machines have a maximum speed of 350 tacts/min. Flat-bed dies ranging from 7 to 12 mm in-line height, using laser technology or grids, and rotary dies with a 0.41 to 1 mm-thick die-plate, magnetic or nonmagnetic, and milled or etched versions have

been developed. Magnetic cutting plates are used for a cutting height of 0.42–1.00 mm, with a cutting angle of 60–100°. The development of form-label combinations where a die-cut siliconized patch transports one or more butt- or kiss-cut paper label forced the development of rotary die-cutting technology coupled with matrix waste removal.

Stanton Avery developed the rotating die-cutting machine. Such machines include a geared die cylinder with bearers and an anvil-roll assembly. Flexible dies that wrap around a stainless cylinder containing magnetic inserts are less expensive. Such flexible steel-strip cutting knifes have been known in the cardboard industry since the 1930s. Rotary die-cutting machines can cut cardboard as thick as 200–500 μm [55].

The clearance and tolerances of rotating die-cutting machines depend on the nature of the material to be cut. The critical cutting range, that is, the usable clearance for common materials, is about 0.010–0.015 mm. The range for cutting through PE films or nonwovens is about 0.005 mm. Cast PE exhibits better die-cuttability and precision registry than blown PE film.

As discussed in Ref. [54], cutting and die-cutting depend on the solid-state components of the laminate (face stock and release liner). Their quality and combination are very important. Good die-cutting is provided by a uniform caliper densified paper liner. Die-cuttability tests have been carried out using PE,PE/PP, PET and PET/SiO_2 and paper (80 g/m^2) as liner and face stock material to test cutting knife wear [57]. The influence of the face stock material and release on die-cutting was studied with rotary die-cutting by Hartmann et al. [58]. The investigations demonstrated the importance of an appropriate release liner for each face stock material, depending on its cutting and tear mechanism. The versatility of the release liner as a cutting basis depends on its chemical nature, mechanical properties, and dimensional tolerance.

The thickness and density of the paper used as face stock material are less important [57,58]. Paper can be compressed and split. Therefore, in paper cutting the deformation of the cutting tool is minimal, cutting forces are minimal, and adjustment of the cutting tool is easier and stable. Cutting of PE includes splitting and separating of the split polymer into two separate phases. Because of the plastic flow of the material, there is a need for a hard bottom surface, with low dimensional tolerances and no compressibility. In this case, cuttability (its quality and speed) depends on the density of the release paper used. Kraft paper is not recommended as a release backing for PE labels. The best results are obtained with high-density glassine paper and PET. Taking into account compressibility- and cutting mechanism-related considerations, it is evident that adequate material combinations of face stock/release liner lead to the best die-cuttability results.

Cutting of PET is similar to that of paper. It is a crack- or slitting-dependent process, initiated at the first contact points between the knife and the PET face stock materials (zip effect). Tear resistance influences cuttability also; therefore, in this case, release papers with broad tolerance yield the best cuttability results. Polyester needs a hard but low-quality glassine paper as a release (backing) material. Therefore, the die-cuttability of different face stock materials can decrease as follows: paper > PET > PE, and the versatility of different release liner materials as backing for die-cutting can be estimated as follows: PET > glassine paper > kraft paper.

In general, voluminous and fragile (inelastic) solid-state laminate components improve cuttability. Therefore, postlamination blow-up of the laminate improves

cuttability. According to Ref. [59], a photo-cross-linked acrylic–urethane acrylate formulation used for holding semiconductor wafers during cutting and releasing the wafers after cutting, with enhanced cuttability, can be prepared by cross-linking and blowing up (foaming) the adhesive. Such a releasable foamed adhesive sheet can be prepared by coating a PSA (30%) that contains a blowing agent (e.g., of microcapsular type) as a 30-μm dry layer. Such an adhesive is removable and improves cuttability.

The cuttability of label films can be evaluated by measuring the cutting forces in both the machine direction (MD) and the cross-direction (CD). For optimum die-cuttability, the MD/CD ratio of the measured values must be about 1; that is, the material must be an isotrope. The manufacturing parameters of the plastic film strongly influence its die-cuttability. The choice of blow-up ratio, together with the thickness of the film (for a given formulation), allows the regulation of die-cuttability.

As noted in Ref. [60], current laser technology offers a limited power/cost ratio; therefore, in-line laser cutting is not viable. Because of the thermal effects of the laser beam, several laminates demonstrate undesirable side effects (discoloration of the carrier and differential cutting of paper and liner). More perspectives are given to laser marking, where special foils accept laser marking. In this case, the minimum width that can be engraved is about 1 mm. Thermal die-cutting was developed for pressure-sensitive decals and is based on the different thermal sensitivity of paper and film carrier materials. For instance, a 0.004-in. cutting line heated at 300°C will cut vinyl, but not paper. Blank self-adhesive labels, precut on silicone backing paper, are manufactured also.

10.3.1.3 Perforating, Embossing and Folding

Perforating, embossing, and folding were discussed in detail by Benedek in Ref. [54]. Such procedures used for postforming the carrier material are more important for tapes than for labels. For instance, a carrier for tapes for low-temperature application may have transverse cuts or holes. A carrier material can be perforated along the center line of the long direction and thus is suitable for tying together printer paper. The plastic-based application tapes have PVC, PE, or PP carrier material that can be embossed to lower unwinding resistance (see also *Applications of Pressure-Sensitive Products*, Chapter 4). The preferred material for diaper tapes is PP (50–150 μm) with a finely embossed pattern on each side. Such tapes allow reliable closure and refastenability from an embossed, corona-treated PE surface used for the diaper cover sheet (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

Perforating and microperforating are common operations in the conversion of labels and tapes. Perforating is used mainly to weaken the carrier material to achieve detachability. Label die-cutting, liner perforation, and pin-feed hole cutting (for labels printed on dot matrix printer) are necessary as well and can be accomplished through the use of male/female dies. Various products require such confectioning. For instance, some price labels require perforation for transport; an adhesive tape used for holding together printer paper is perforated along the centre line in the long direction; electrical insulating tapes used for taping may also be perforated. Slits or perforations in the face stock improve the tamper-evident properties of labels (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Common mechanical perforation machines have 25, 40, 50, or 70 teeth/in.

Microperforating can be used to transform some carrier materials in a porous web. Such microporous webs are needed for medical tapes, condensed water-free packages, etc. (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Various methods are used for perforation, such as hot needles, liquid or gas jet, ultrasons, high-frequency laser, and electrostatic microperforation. Hot needles are used for PE and PP films and nonwovens. The hole diameters produced by this technology are 200–500 μm. On such machines webs with a width of 1,500 mm can be processed with a speed of 10–30 m/min. Gas and liquid jets are used for perforating soft webs (foam, nonwovens, board). Thermoplast-like polyolefins and PVC can be cut with ultrasons. High-frequency cutting is limited to thicknesses of 5–30 μm. Laser perforating is used for narrow webs. It allows running speeds of 600 m/min and is used mainly for fine paper. The hole diameters produced using this method are 50–200 μm.

Electrostatic microperforation can be used for electrically nonconductive materials only. The procedure uses electrodes with high voltage and high frequency (500–5,000 Hz). Webs with a width of 50–1,000 mm and weight of 5–100 g/m^2 are processed using this procedure at a running speed of 300 m/min. Paper, plastics (LDPE, PET, PP, and PVC), laminate (PET/PE), nonwovens, and other materials can be processed using this technology. The diameter of the holes obtained is 2–70 μm, the pore number attains 1.6 Mio/m^2, and the interpore distance is 1.0 mm. The reciprocal distance of the stripes is 0.25 mm. Microperforation (hole diameter of 2–70 μm) as well as macroperforation (hole diameter of 50–500 μm) can be realized electrostatically.

Special electrodes allow the manufacture of perforations with a diameter of 2–5 μm using corona treatment. Unlike glow discharge treatments (see Section 10.1.2), this process could be applied under ambient conditions as a continuous method. Flame perforation is used as well; this procedure allows the manufacture of hundreds of holes per square inch, with a hole diameter of 0.4 mm.

Embossing is generally carried out during the manufacture of plastic carrier films [1]. Embossing of metal films, metallized PE, and paper is carried out more easily and runs at much higher speeds (up to 400 m/min) than that of PE. Microembossed films are used for image holograms, two- and three-dimensional background designs, decorative laminates, and labels. Embossing is a converting operation used for self-adhesive wall coverings. Embossing allows modification of the surface geometry. Such modification is required to regulate the debonding performance characteristics. Embossed paper or film provides mechanical release. Such embossed carrier materials are used for diaper tapes, medical tapes (see *Applications of Pressure-Sensitive Products*, Chapter 4), wall covers, decor films, etc. Room temperature and high-temperature embossing can be carried out. For instance, PVC wall covers have been embossed using high-temperature (120–140°C) embossing.

Folding is used mainly for computer-printable labels and tapes. A special application apparatus is suggested for folded tapes. Folding along the longitudinal axis is proposed to prevent back-rolling of the tapes. Labels can be either rolled or fan folded. Special pharmaceutical labels can have (folded) take-off (detachable) parts as well, to allow multiple information transfer. Parts of the label remain on the drug or on the patient. Such construction is perforated to allow multiple detachment (i.e., multiplication) of the labels (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

10.3.2 Other Conversion Methods

Conversion includes the postprinting of confectioned PSPs and mechanical and chemical processes for special PSPs.

10.3.2.1 Printing

Printing of the full-width web is a common operation for tapes and protective films. Postprinting is specific for labels. Postlacquering is required for special label applications only. Narrow-web printing offers the advantage that it can be used for other operations; that is, users can modify or attach a variety of nonstandard devices to manufacture different products.

Printing is the most important nonmechanical conversion procedure. Printability includes quite different performance characteristics such as lay flat, dimensional stability (under various mechanical and environmental stresses), good anchorage, and adequate machinability (see also *Applications of Pressure-Sensitive Products*, Chapter 8). When choosing a printing base, certain parameters such as required quality standards, performance ratio, and subjective assessment of the finished product must be taken into account. Quality includes printability, roughness on the front and reverse sides, gloss, opacity, density, thickness, tensile strength, and bending stiffness. Good printability requires low surface roughness, more or less surface absorbancy (depending on the printing ink), sufficient surface energy, resistance to solvents in printing inks, resistance to heat produced during ink drying or hot foil stamping, and the absence of separating agents and other impurities from the imprintable side.

Printing was discussed in detail by Benedek in Refs [7,54]. Various printing-like conversion technologies exist and the materials used in these processes must fulfill technological requirements. For instance, predecoration of packages involves graphic application before a container is filled with a product. This method is used by bottle manufacturers and contract packagers. Predecoration methods include application of a label in the package mold, direct-screen printing on the container, hot stamping, heat-transfer decoration, a shrink-sleeve system, and pressure-sensitive systems (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Decoration can also be applied in-line with filling.

The importance of printability differs for various PSP product classes. For labels it is determinant and differs according to the label-application domain. For instance, printing of labels is most important for extended-text labels (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Aesthethic products such as labels, or certain tapes, and those carrying information must be printed with a high-quality image or text. Resolution (the minimum distance between two objects giving a clearly separated image at a given magnification for a given optical system) is one of the main characteristics of a printing procedure used as a criterion by the choice of printing method.

Printability of the laminate was discussed in Ref. [7], where lay flat and dimensional stability were described (see also *Applications of Pressure-Sensitive Products*, Chapter 8). General and special printing considerations, together with performance characteristics of the main printing methods used for PSPs, and special printing considerations (e.g.,

printing of plastics and nonpolar carrier materials) were discussed. Special printing parameters should be taken into account depending on what carrier material is used, the product class, and the type of ink. Printing-related performance characteristics of the carrier material (e.g., shrinkage, lay flat, smoothness, stiffness, elongation in printing, and wrinkle build-up) were discussed in detail in Ref. [54]. Flagging or wing-up of labels on curved surfaces was described in Ref. [7]. Printing properties depend on the substrate to be printed. In choosing a carrier material and a printing technology, the composition of the printing ink should be taken into account. Reciprocal influences exist between the printing ink and the paper or film. Printing quality depends on the surface finishing, roughness, and wettability. Such properties are affected by web preprocessing (see also Section 10.2.2.3). For instance, for papers printed using the direct-thermal printing method, the choice of the paper (non-top-coated or top-coated) can be dictated by the method of preprinting. Non-top-coated grades have less protection against solvents or monomers. Therefore, water-based or low-solvent flexoprinting are the methods best suited to this grade. Top coating influences UV printability also. Top-coated papers can absorb the monomers in UV-curable inks. The nonabsorbancy of films must be compensated for by the proper choice of ink and drying conditions. Inks for normal and thermal papers and for nonabsorbent carrier materials such as aluminum, PVC, and PP have been developed.

Most PSPs are plastic based. The printing of plastics is a special domain in which electrostatic charges, lack of porosity, high surface tension, thermoplasticity, sensitivity to solvents, and environmental stress cracking are the main problems. Curling and shrinkage are also problems that appear during printing of films, partially as a consequence of the printing process (see also *Applications of Pressure-Sensitive Products*, Chapter 8). The smoothness of the surface can also affect the bond. The rough and porous surface of paper provides some mechanical adhesion, whereas the smooth surface of film does not. Surface energy determines wetting and also influences bonding, and printing of nonpolar plastics with water-based inks causes additional problems.

The chemical composition of the film substrate affects the bond. Additives (compatible or migratory) in the polymer can also influence the bond. Lower-molecular-weight oligomer fractions from the polymer can also cause problems. For instance, LLDPE sometimes contains more low-molecular-weight species and will require more antiblock additive to prevent blocking. Surface-active agents create an adhesively weak layer. Excessive additives on the film surface (e.g., slip and processing aids) can cause printing problems. Residual oil on the film surface is also dangerous. Static electricity may cause printing and handling problems of plastic films; therefore, before being coated with varnishes or lacquers, a plastic surface must be pretreated with antistatic agents to deionize the air. It is recommended that static charge elimination systems be placed after the printing cylinders to help dissipate charges (see also Section 10.2.2.1).

Nonpolar carrier materials are difficult to coat. In some cases, a top coating is applied before printing. According to Waeyenbergh [61], good ink anchorage is achieved for OPP by the choice of suitable ink and lacquer, adequate drying capacity, film surface finish (pretreatment level or primer), and corona treatment on the printing press. As known from printing practice, different plastic films display different degrees of printability. For instance, acetate films display good printability and can be used as label or

tape carrier materials. A 50-μm cellulose acetate film needs no pretreatment for normal printing and is computer printable also. PP is an alternative for PET for "no-label look" labels (see also *Applications of Pressure-Sensitive Products*, Chapter 4). For such products a 60-μm PP film is used. The film is coated with a lacquer to allow printing by screen printing (solvent based and UV cured), flexoprinting (water based, solvent based, and UV cured), and UV-cured letterpress printing. For polystyrene films, flexography, roll-feed lithography, and gravure printing are recommended.

For PVC and vinyl chloride copolymers solvent-based gravure and flexoprinting inks have been suggested. For instance, PVC seal tapes can be printed using sandwich printing (flexoprinting for the top side and gravure printing for the back side between the film and the adhesive).

Printing inks generally consist of two basic components: pigment and vehicle. Vehicle systems contain film-forming parts (resins and oils), volatile materials (solvents, water, viscosity regulators, etc.), and additives (plasticizers, dispersing agents, drying agent, etc.). Different printing processes need different inks of various compositions and rheology. Gravure, flexo, and screen printing use low-viscosity inks and simple inking systems. Lithographic and letterpress systems use printing ink with higher viscosity and a complex metering system. Flexographic inks are low-viscosity recipes based on water or alcohol, with nitrocellulose, PVC, or PUR as base polymeric components. Lithographic inks are water-soluble high-solids compositions. Gravure inks are solvent-based high-viscosity compositions.

There is a growing interest in printing technologies such as gravure printing and flexoprinting that use water-based inks. There are differences between the characteristics of water-based inks and those of solvent-based inks. Apart from the fact that different resins and pigments are used in their formulation, major differences arise from the physical and chemical properties of water and organic solvents. These differences concern the boiling temperature, evaporation rate, evaporation heat, and surface tension. The surface tension of water is much higher than that of most other solvents, and therefore it displays lower wettability. Water-based gravure ink requires cylinders with small cell volumes. The same approach has been confirmed for flexoprinting through the use of ceramic anilox with line screens.

Different printing procedures use different solvents and drying temperatures and, thus, they cause different stresses in the web. Therefore, printability is a function of the carrier thickness. For instance, gravure printing is suggested for PE films that are at least 25 μm thick and for PP films with a minimum thickness of 12 μm. Printability depends on the surface wettability, that is, the degree of treatment. The grade of film also influences pretreatability (see also Section 10.1.2.3). The loss of treatment effect also depends on the nature of the film (see Section 10.1.2.3). For instance, blown films maintain their degree of treatment for a longer period of time than cast films. Triboelectricity affects printability as well. As known from printing and web handling, polyester displays a high level of triboelectricity.

A great number of different printing methods exist. The main procedures use impact printing (e.g., flexo, gravure, screen) or nonimpact (e.g., ink jet, laser, thermotransfer) printing. The requirements concerning the carrier material for these procedures are quite different. For instance, nonimpact printing procedures need paper that has

a porous surface. The use of such printing methods is also related to their versatility to broad-web or narrow-web printing. Narrow-web printing is made after confectioning and is carried out more and more by the end user. Narrow-web label postprinting machines use impact printing methods such as offset, flexo, or dry offset printing [61]. Printing machines (drop on demand, thermotransfer, and laser) of various suppliers are listed and examined comparatively in Ref. [62]. Drop-on-demand printing devices are used for product coding. Such machines print logos, barcodes, autodating, numbering, and graphic programs at a printing speed of up to 5 m/s. Thermotransfer printers run up to 600 mm/s at 300 dpi. They are used for printing on thermo labels, paper labels, PE/PTE, PE/PP, PVC, PET, cardboard, cellophan, and aluminium labels up to 2,500 sign/s.

10.3.2.1.1 Label Printing

Label printing was described by Benedek in Ref. [34]. As discussed previously (Section 10.2.2.4.2), label manufacturing includes web printing and label overprinting. Label overprinting is really a conversion step required to memorize supplementary, variable data on the label. Because the printing of labels is the most exigent domain of PSP printing, a short description follows about the main features of different printing techniques used for labels. For label printing various printing methods such as letterpress, flatbed, semirotary, rotary, flexography, lay and rotary offset, lithogravure, screen, hot foil, nonimpact, and digital printing, etc., are used (see later). The choice of method determines important parameters such as reduced set-up times, high production speed, and the ability to change sizes without changing cylinders. The choice of the best printing method depends on run length, quality of printing required, type of equipment available, and sheet or web form.

The type of adhesive and the end use of the printed item influence the printing method as well. As an example, sandwich printing is usual for plastic labels coated with hot melts. These have a transparent PP or PET carrier and an OPP release liner. Rating plates (see also *Applications of Pressure-Sensitive Products*, Chapter 4) can be sandwich printed also, with the reverse side of a transparent material printed with mirror lettering.

As mentioned above, printing methods can be classified as impact and nonimpact. Classic, mechanical printing technology uses impact printing. The most important impact printing methods are letterpress and flexographic printing. In Europe, letterpress, flexography, and screen printing of labels are preferred. Screen printing should be used for more expensive (quality) labels than flexo or letterpress printing.

In gravure printing the image is etched into the metal cylinder. The wells are filled with ink, and the excess ink is wiped off with a doctor blade (see also Section 10.2.1.2). In this procedure, the pressure of the knife on the cylinder attains 12 N/mm^2 (i.e., 2,100 atm). Gravure-printing presses for labels must secure excellent printing quality and productivity, as well as the possibility to perform all other converting operations required for labels such as lamination and die-cutting, in-line with the printing. The printing cylinders are cleaned with special burst cylinders.

In-mold labels are competitors to pressure-sensitive labels (see *Applications of Pressure-Sensitive Products*, Chapter 4). In-mold labels require gravure printing, sheet-set offset gravure, narrow-web UV, special inks, and special die-cutting.

There is a general trend in the packaging industry to replace gravure printing with flexo- and offset printing. In the United States, flexoprinting (flexography) is the main label-printing procedure [63]. Flexography is a form of web-fed (letterpress) printing. This technology uses flexible (rubber-like) printing plates mounted on a printing cylinder. The print pattern is raised, and the ink is applied only to these raised portions. In-line, stack, or central-impression flexo are the main machine configurations. Flexoprinting of films with one-cylinder printing machines requires high cylinder precision and web regulation. The classic flexoprinting uses four cylinders in the printing device. An ink-transport cylinder transfers the ink to the gravure cylinder. The gravure cylinder transports the ink to a plate cylinder that has a soft printing plate (stereotype). A pressure cylinder ensures contact with the web. The first generation of flexoprinting machines used solvent-based low-viscosity printing inks, giving low-quality printing. In the 1980s a new generation of rotary flexoprinting machines was developed. For labels a common flexorotary press has one to three printing devices, a die-cutting device, a winder for labels and waste material, and a lamination device. Common flexoprinting inks for labels are based on alcohol or water, with a maximum of 3% solvent. Flexopresses for overprinting labels can print in eight colors, have a 420- to 620-mm web width, and run with at a speed of 150–200 m/min, depending on the carrier material [64]. Narrow-web (420–620 mm) flexoprinting machines can use webs with a thickness of 20–300 μm [65]. Flexo postprinting machines are suitable for producing screen rulings of up to 60 line/cm [66]. UV drying was developed for flexoprinting as well. Switching to UV-curable inks from solvent-based inks increases the printing speed by up to 20% [67]. The introduction of UV-cured inks allows flexoprinting on different, nonpaper substrates printed originally with letterpress machines. Water-based and UV-cured printing inks give a seal-resistant (over 200°C) image. Such a printing machine typically has a flat-bed and rotation die-cutting and UV-lamination equipment.

Screen printing is the least technologically advanced printing method, but it can be used for the greatest number of types of substrates. It can be combined with other printing methods such as letterpress printing and hot-foil stamping, and it is recommended for plastics. The main market segment for screen printing includes food, pharmaceuticals, cosmetics, toiletries, and household uses. Rotary-screen printing machines have been in use since 1986; they run at 50 m/min [68]. According to Ref. [69], rotary-screen printing was developed earlier, in the 1970s. Today it allows running speeds of 30 m/min, tolerances lower than 50 μm, and printed areas of 5 m^2. Materials with different thicknesses, for example, PVC films with a minimum thickness of 0.1 mm, PET with a maximum thickness of 350 μm, and hard foams with a thickness of maximum 20 mm, are printable using screen printing. Posters, labels, membrane switches, and transfers can be manufactured with this method. Weather-resistant decals are also printed using screen printing. For this procedure the drying time is short and energy costs are low, but there may be register problems. Special rotary-screen printing machines were developed for labels. Reel-to-reel screen-printing lines allow labels to be printed with a production capacity of 10–20 m^2/min and a web width of 150–750 mm. For instance, screen-printed polycarbonate labels are used for in-mold labeling. Laminators, embossing units, die-cutters, sheet-fed dryers (sheet fed from a roll) can be attached to the printing press.

There are two basic types of lithography, direct and offset lithography. In offset lithography the image and the imageless area are in the same plane. The image area

is oil-receptive and hydrophobic, and the inks adhere to this portion. The imageless area is hydrophilic. In commonly used offset lithography the image is transferred with a blanketed rubber offset cylinder. Offset printing allows a resolution of 2400 × 2400 dpi. Offset printing has some disadvantages: in roll-offset printing the humidity content of the paper may decrease from 5–7 to 1–2% during drying, which causes dimensional changes; excessive running rates can cause cylinders to overheat and deform (bomb) due to the high dilatation coefficient of plastic sleeves. This deformation produces printing defects. Offset-printing machines (sheet) can be used for lacquering as well. Special offset-printing methods use a water-free offset-printing plate.

Letterpress printing is largely used for labels. Flexographic printing is growing as well, but the main printing method is letterpress printing [70]. Rotation letterpress machines were developed. They are complex equipments with numerous cylinders and stable construction, so they are more expensive than common flexoprinting machines. So-called short-roll-train coating devices have also been developed; these constructions have only three cylinders. Here, a special gravure cylinder transfers the ink to the soft-plated cliché cylinder. Through letterpress printing, labels are printed at 60 lines/cm, at a running speed of 60 m/min. Such machines can have UV-drying units also. For letterpress-printing machines with UV curing, numerous (15–20) cylinders are used to transport the highly viscous, UV-curing printing ink to the hard printing plate. In this case, web contact is ensured by a soft, flexible pressure cylinder.

Tampon printing is an indirect gravure printing method. The image is transferred from the (steel) gravure plate with the aid of an oval or circular rubber pad [71]. Tampon printing has been in use since the mid 1970s. It allows on-the-spot printing of nonuniform, nongeometric surfaces with small details at high running speed. It is less expensive than screen printing or hot stamping.

Mask printing can be used for direct imaging also. Here the printing tool (mask) is a perforated carrier, and the ink penetrates into the perforations [72]. The mask, or master, is manufactured using a thermal procedure in which a PET film is perforated with the aid of a computer-controlled thermal head, giving a resolution of 400 dpi. The master is used by a scanner and an image processor for printing or modifying the image before printing.

Hot stamping is a lithographic printing procedure that uses predried ink. It possesses similarities with embossing and in-mold labeling (see also *Applications of Pressure-Sensitive Products*, Chapter 4). It may be considered a dry-lamination method. The printing tool is electrically heated. During hot stamping the image is transferred with a pressure of 100 kN at a temperature of about 120–160°C onto a surface of 150 × 250 mm [73]. Hot stamping allows protective lamination too and is used often for labels. This is a one-shot operation; no intermediate drying steps are necessary, common inks can be combined with partially metallized inks in the same image, different surface structures can be combined, and fine color nuances are obtained. The substrate must not have a geometric form, but various substrates can be used. The ink for this procedure is less expensive than the transfer film. It has the supplemental advantages that there are no problems with pretreatment; because no solvent is used there is no problem with solvent sensitivity and no pollution; and a metallic effect can be achieved (such an effect is achieved currently by metallizing only). No registry problems appear.

There are two different types of hot-stamping printing machines: one with a stamping cylinder (for circular or flat printing) and the other with a flat device. The circular/flat principle ensures a continuous laminating on a large surfaces without air bubbles and overheating [74]. Different types of hot stamping exist: plane, with structure, and with relief. Hot stamping can be considered a special case of embossing.

The first German patent concerning hot stamping appeared in 1892 (granted to Ernst Oeser). Today, materials of this type are used in many variants of color and processing methods. Hot stamping die-cutting machines have been developed as well. These systems offer the possibility to produce decorative labels, resistant type plates, and informational labels. Depending on the specified requirements, the machine can be equipped with various work units (stamping station, numbering station, laminating station, and die-cutting station). Longitudinal and cross-cutting devices are used. The machine has a head for printing and a head for die-cutting). Generally, material is processed in reels. Hot-foil labels are printed at a rate of more than 10,000 impressions/h.

Hot stamping can be used for in-mold labeling also (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Because of the high temperature and pressure used in this procedure (in-mold labeling is carried out with a molten adhesive), it may be considered a case of hot stamping.

Hot stamping of holograms is a very complex, high-speed (70–90 steps/min) procedure that requires images to be exactly positioned. Hologram hot stamping was developed in 1986. Hot stamping of holograms is adequate for the transfer of holograms with a replica of the image on the stamp. It requires very exact placement of the image. Single-pass holograms have been developed that allow holograms to be created in-line on any narrow-web press. Such a process uses a patented plastic imaging foil with a 20- to 100-μm thick metal layer that adheres to the label stock during the stamping process through a lacquer and a heat-activated adhesive. Hot stamping and embossing the foil directly on the machine eliminate the security risks [73].

Holography was discovered by Dénes Gábor in 1948, but the first holograms that could be seen in white light were not developed until 1963. The retrievable storage of holograms was achieved in 1980 by embossing, and transfer of multiple embossed copies of holograms was developed in 1984. The main steps in the printing of holograms are manufacture (mastering) of the hologram, replication of the master hologram, and transfer of the replica. The master hologram is used to prepare the shims, the embossing tools for hologram transfer. The hologram on a special fotoresist is coated with a nickel layer; this is the master embossing tool. Two methods are used to transfer the holograms: the hot-stamp method and PSA lamination. With a special, rotational embossing system the holograms can be transferred using a nickel embossing tool on a film for hot stamping. The carrier film should display tear resistance; therefore, a 19- to 23-μm PET is recommended as transfer film for hot stamping. This is a metallized film coated with a special lacquer that can be embossed. PSA labels can be "printed" with holograms using hot stamping or a PSA hologram. Diffraction films are made using the same procedure. They contain two-dimensional images only. Pressure-sensitive holograms can be laminated, cut, and overprinted. For pressure-sensitive holograms a 50-μm PET has been used. In 1984, a special method was developed to permanently bond holograms onto a substrate for use as identification. Hot-foil hologram presses can apply up to four

holograms in one pass up on a web up to 250 mm wide. Label manufacturing machines are completed with hologram-dispensing units, allowing the application of 70–90 pieces/min. For advertising and promotion, pressure-sensitive labels with holograms play an important role. They are die-cut on the roll, have various carrier materials, and are used for direct mailing. If they have a sandwich build-up, using a transparent cover film, the label can be separated in two parts, with one carrying the technical (hidden message) information [74].

Various other products are based on the principle of hot stamping. For instance, transfer films are hot-stamping films applied to large substrate surfaces. They have a PET or PP (coex or oriented) carrier and a flexible and conformable ink composition. Heat-transfer decoration uses a preprinted paper carrier that transfers the graphic image onto a treated container using a thermal applicator [75].

Cold-foil transfer may replace hot stamping in certain applications. In these cases a special adhesive is used to fix the image on the carrier. The adhesive is cured with an UV-curing system with a time window for lamination. In this case, a special cold-lamination head transfers the image on the substrate [76]. In this manner, laminating of photos on labels can be carried out as well.

Label overprinting uses various procedures working with impact and nonimpact printing, such as mechanical printing; dot matrix, electronic and computerized printing systems; direct thermal and thermal transfer; ink jet, laser, ion deposition, magnetography, and digital color printing. Direct thermal printing is the largest segment, followed by methods that use a toner (e.g., laser, ion deposition, EB, and magnetography). Ion deposition works like a copier, but uses increased pressure for toner absorbance. It has been used in the label industry since 1983 and prints at a speed of 90 m/min [77].

Nonimpact printing methods allow low noise level, high speed, and high printing quality. The main nonimpact printing methods include electrostatic and electrosensitive procedures, magnetography, ink-jet printing, and thermography. Universal product codes (bar codes), which use nonimpact printing, are a major reason for the industry's growth, because their use has increased at a rate of 25–50% per year. Digitized variable image printing (VIP) allows customer data supplied on various media to be downloaded, manipulated electronically, and printed. Variable information printing (see later) allows the manufacture of personalized labels in very small quantities (for example, 100–500 pcs) [78].

Dot-matrix printing is an older printing method that may be used for "low-density" bar codes only. Its resolution is limited at 150 × 150 dpi and it uses a colored ribbon. It is an impact printing method that mechanically embosses the ink layer into the carrier. Because of its liquid state, the ink can rapidly bond chemically with low-energy plastic surfaces. Very good chemical, weathering, and abrasion resistance is given. Unfortunately, this procedure is very noisy, and the resolution of the image is low.

Thermal printing, which uses heat to color the face stock, comprises direct thermal printing and transfer thermal printing. Direct thermal (thermosensitive or thermochemical) printing applies a heat-sensitive printing material, which undergoes a color change when heated. This method of printing was developed in Japan, for facsimile paper, in the early 1970s. For instance, a direct thermal printable label may have a

five-layer construction. The paper carrier is coated with a top layer that includes a heat-sensitive ink embedded in a lacquer. Some labels also have a protective overlayer. For direct thermal printing, special paper is required. Common organic direct thermal printable papers include a colorless leuco dye and an acidic color developer. These are coated and held onto the surface of the paper with a water-soluble binder. During printing, the two components melt together and react chemically to form the color. To limit this image to the heated area, inorganic fillers (e.g., calcium carbonate, clay) are used. The problem of image stability (protection against chemicals) is solved by applying a top coat as a transparent film-forming layer. It is also possible to apply a barrier coat to the underside of the paper to prevent adhesive or plasticizer migration from the opposite side. These papers are classified as non-top-coated (nonsmudgeproof) and top-coated (smudgeproof) papers.

Thermal transfer printing is a 20-year-old technology, created by the Kenjay Company [79]. In thermal transfer printing there is a thermal print head (which is rapidly heated and cooled again) and an ink-transfer ribbon. The ink coated on the PET film is solid at ambient temperature. Under the heated print head, the ink becomes fluid and is transferred from the film to the paper. High-speed printing $>$ 1,000 mm/s is carried out using this technology. The method does not use a heat-sensitive label stock.

Thermotransfer printing for labels is used for different substrates (paper up to 300 g/m^2, PET, PVC, fabric, etc.). Materials weighing up to 350 g/m^2 can be printed. This method allows printing of "high-density" bar codes. Thermal transfer printers with a near-edge type printing head allow a resolution of 300 dpi (12 dots/mm), with a 10-mm print-free area and a running speed of 250 mm/s. Thermal transfer printing is used for price-weight labels (see also *Applications of Pressure-Sensitive Products*, Chapter 4) and computer-printed tamper-evident labels (see also *Applications of Pressure-Sensitive Products*, Chapter 4). High-speed, high-resolution thermal printers are capable of printing bar codes in either picket or ladder form. Thermal transfer printers are used for rating plates also (see also *Applications of Pressure-Sensitive Products*, Chapter 4). Their resolution is 7.6–11.4 dots/mm and their printing speed can reach 175 mm/s. Although this printing method was developed for paper labels, the ink does not penetrate the paper; thus, its chemical resistance and abrasion resistance are relatively low. Fanfold material can also be processed using this procedure. Single labels, strip labels, and label strips can be printed. Labels with a width of 30.2 to 164 mm cover almost all areas of application. Within recent years the technical performance characteristics of thermotransfer printing machines have been improved substantially. According to Ref. [80], thermotransfer printing presses work with 150–600 mm/s and give a resolution of 300 dpi. Depending on the need for smudge or scuff resistance, wax-based, resin/solvent, or multicoated ribbons are used. Compatibility guides for thermal-transfer ribbons and pressure-sensitive films summarize the test results for ribbon and substrate combinations, such as speed, burn setting, print quality, smudge, scratch, and chemical resistance [81].

Presses for printing a small series of labels (20,000 pieces) are recommended for color thermal-transfer printing. They run at a speed of 100 mm/s, have print dimensions of 240 $\times$ 374 mm, and can cut and perforate. Such presses produce tractor punching and transverse cut. A resolution of 300/400 dpi is achieved.

Electrostatic printing is based on the same principle as xerography and electrography. Both give an invisible, latent image. Xerography uses an intermediate image carrier. The main electrostatic procedures are electrophotograpy and electrography. In electrography the image is built up directly on the substrate to be printed with charges. Laser, LED magnetographic, and EB devices generate a latent image onto a photoconductive drum.

Direct charge imaging is a belt type of imaging system. It is a toner-based printing method, where imaging is given by a continuous and seamless dielectric belt, rather than a photoconductive drum.

This belt carries the latent image. Fusing is accomplished with heat. This method allows (theoretically) running speeds of 300 m/min with 1200 × 1200 dpi resolution.

Electrophotography builds up the image using light and an electrically charged substrate. The image is made visible with the aid of a toner. Electrophotography is laser printing and uses toner to fix the image.

With laser printing based on electrical conductivity, the image is given by selective discharge of the image carrier material by laser beam and thermal fixing of the image. A laser cartridge generates a charged printing "form" onto a rotary light-sensitive cylinder, which attracts the toner [82]. The toner develops the image, which is fixed by fusing, or pressure. Such methods completely reimage the cylinder after every impression. The image is built up by a raster image processor; a laser beam writes the image form the computer onto a drum. The laser beam can be applied to burn out the image in a two-layer laminate. Laser printing allows a resolution of 600 × 600 dpi and requires temperature-resistant laminate components. The use of temperature for fixing limits the choice of carrier materials. Therefore, only high-temperature-resistant carrier materials such as PET can be used, and temperature-resistant, high-melting-point tackifiers should be used for the adhesive formulation (see also Chapter 8). Laser-printable labels (sheet) are warranted for 4 years and may be used between −20 and +120°C. On the other hand, the chemical resistance of the printed image is low. Modern laser-printing machines print 2,500 characters/s. Desktop laser printers allow a printing speed of 4–20 pages (A4)/min, whereas printers for big computers achieve 75 pages/min [83]. Laser printing is used for printing overlaminated labels as well.

An EB printing system is used for high speed in-line application of variable data. With an EB printing system (variable image printing) the numbers, text, graphics, etc., can be printed using a computer program. They can be oriented in any direction. The resolution of the method is 300 × 300 dpi. Electron beam printers run at a speed of 100 m/min. The machine is based on a cold-pressure-fusing technique that presses the dry toner into the substrate. A fastening is recommended to ensure adhesion without smudging or flaking. Varnishing, UV-cured lacquering, or lamination are suggested.

The electrosensitive method uses an electrolyte as the base substrate. Electroerosion printers exist as well; they work on a metallized substrate. Magnetography applies magnetic fields for image conservation.

An ink-jet (or bubble-jet) printer has small (0.03–0.06 mm), ink-filled channels that are heated, with the heating controlled by computer. The molten ink bubbles are directed by electrical charges (and an electric field) to build up the image. Because of the fluid state of the ink, this procedure can be used for rough surfaces also and needs a porous

substrate surface (or top coat) and a long drying period. The resolution of the image is low. Bubble-jet printers allow digital printing with a speed of 150 mm/s and a resolution of 150 × 150 to 360 dpi. Ultrahigh-speed ink-jet printing systems have been designed to print at speeds of up to 300 m/min and allow printing of 1,800 characters/s.

Digital printing is used in many cases where parts of the printing equipment are computer controlled. Digital printing is actually the digital build-up of the printing image onto a printing tool with the aid of a computer. This is the computer-to-machine or direct-imaging technique. Currently, direct imaging is applied in electrophotography or offset printing (see above).

Some years ago, digital printing was carried out primarily on paper and was available only in black. Now the options range from black to as many as six colors on paper and film. Available technologies include dot matrix, color laser, thermal digital printers, or color copiers. Computerized digital label converting equipment can print and die-cut labels.

Digital-offset technology was developed to satisfy the demand to increase the number of colors used for printing labels. Digital offset is a combination of offset printing (see above) and xerography. The print image is digitally built up and transferred to an image cylinder. The electrostatic-charged printing ink is transferred from this cylinder to the rubber image-transfer blanket and from there to the carrier material. Recently, one-shot color technology was developed. The advantages of the system are the following: there are no register problems, the printing quality is regulated in the preprinting step (therefore, it is possible to use less dimensionally stable materials), no drying system is necessary, no changeover in printing is necessary if new products are needed, no printing plate (form) manufacture is required, and there are no machine parts that depend on product geometry. This procedure is recommended for production runs of less than 100,000 [84]. This is a flexible system that allows (at least theoretically) a new image for every cylinder rotation and a printing speed of 100 sheets/h. The material used for digital printing must have an electrostatic-receptive surface, heat-resistant adhesive, and resistance to humidity changes. Running speeds of more than 10,000 impressions/h are claimed; the common construction is a machine with three heads, two for printing and one for cutting.

For label printing by flexography, letterpress, or screen printing, UV-curable inks have also been developed. Special so-called cold-UV systems have been introduced that work with only a low level of thermal (IR) radiation [65]. Cationic printing inks have been tested industrially in Europe since 1993. Free-radicalic UV-curable systems contain acrylics as the base macromolecular compound. Cationic UV-curable systems include low-viscosity epoxides. Both are 100% solids in comparison with common, solvent-based inks, which have 30% solids.

Important growth in the label industry has come from blank labels or nearly blank labels, for which more printing is done at the point of use. Therefore, combined printing methods have been among the main processes used in Europe (letterpress, flexo, offset, and digital printing). Actual label postprinting machines for paper labels can use 19 formats, have software to change it, and print up to 32 labels/min using various software (e.g., MS-World, MS-Outlook, or Palm-Desktop) [85]. VIP and product information printing labels today make up more than half of all label usage and are still growing in volume terms worldwide at around eight times the rate of any other method of labeling [86].

10.3.2.1.2 Printing of Tapes

Printing of tapes is discussed in Ref. [54]. For printability of tapes the carrier must possess contradictory performance characteristics. Its surface must be abhesive to ensure release properties (i.e., low unwind resistance), but at the same time it must exhibit good affinity to the printing inks and ensure their anchorage.

Like labels, tapes can be printed by various printing methods, such as gravure, flexo, offset, or screen-printing procedures. Tapes with OPP carrier were printed first with solvent-based printing inks. Water-based technology was developed toward the end of the 1980s. The most used printing method for tapes is flexographic printing. Chrome-plated steel gravure cylinders with 60–100 engraved pyramidal cells/cm^2 are used together with steel or plastic (polyamide) blades. A decade ago the majority of tapes (70%) were only one color. Now the main part of tapes are printed with multiple colors. Common three-color printing machines for tapes have a width of 100–300 mm and run up to 200 m/min.

Seng [87,88] discussed the printing of PP tapes using UV-cured flexoprinting inks. Generally, radiation curing uses UV light, x-ray radiation, and EB that are capable of breaking the C–C, C–H, or C–O links (i.e., have an energy of more than 3.6–4.3 eV). Classic radiation-induced curing of printing inks is based on microwaves and IR radiation. In UV-light-induced curing, ionic (cationic) and free-radical polymerization can be used. Cationic initiators are onium salts that give by photolysis an acid. The UV-light absorption domain for most cationic systems is situated at 275–450 nm (see also Chapter 8). Good results are obtained with inks based on cycloaliphatic epoxides (chain opening polymerization by oxirane rings). Ionic UV systems possess the advantages that they are not inhibited by oxygen, and they result in less shrinkage (see also Chapter 10) and less toxicity. Unfortunately, such systems are less reactive, react more slowly (curing is not finished after radiation; thus, postcuring is necessary), and exhibit lower penetration. Therefore, double-cure (dual cure) systems are also proposed. In this case, a peroxidic initiation is followed by UV curing.

10.3.2.1.3 Printing of Protective Films

Printing of protective films was discussed by Benedek in Ref. [54]. Generally, protective films do not carry information. They are printed for opacity, as a technological aid, or for publicity. Flexoprinting is generally used for protective films. In special cases, gravure or screen printing is applied. Taking into account that certain protective films (e.g., films for protection of plastic plates) are postprocessed (together with the protection film), printing inks used for protective films must support the elevated processing temperatures. For instance, inks used for protective films for polycarbonate plates must be resistant up to 160°C. The ink must be compatible with the protective lacquer on the mask and should not penetrate through the masking during cold- or hot-line bending of the sheet and during drape forming.

Diversification of the application fields of PSPs leads to new conversion methods of the PSA and PSP. Such methods are used mostly for sophisticated products, such as business forms, medical, or pharmaceutical labels, radiofrequency identification labels, and PSAs used in electronics, where special build-in, dosage, or application

methods are used for PSAs. For instance, flexographic varnishing units, plough folders, spot and pattern gluing modules, self-sealing adhesive modules, and card and label applicators can be associated with the main printer. Such equipment can be used to produce forms also. Batcher stackers (with chipboard inserters) and wrapping machines complete the equipment (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

10.3.2.2 Special Conversion Methods

For special PSPs various other conversion methods are also used for finishing. The main part of such processes concern surface finishing by metallizing and overlaminating.

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11

Pressure-Sensitive Adhesives Based on Polyurethanes

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11.1 Introduction

An adhesive is a compound that adheres or bonds two items together. Adhesives may come from either natural or synthetic sources. Some modern adhesives are extremely strong and are becoming increasingly important in modern construction and industry [1].

The first adhesives were natural gums and other plant resins. Archaeologists have found 6,000-year-old ceramic vessels that had broken and been repaired using plant resin. Most early adhesives were animal glues made by rendering animal products, such as the Native American use of buffalo hooves. Native Americans in what is now the eastern United States used a mixture of spruce gum and fat as an adhesive and as a caulk to waterproof seams in their birchbark canoes. During the times of Babylonia, a tar-like glue was used for gluing statues. Egypt was one of the most prominent users of adhesives. The Egyptians used animal glues to adhere tombs, furniture, ivory, and papyrus. The Mongols used adhesives to make their short bows. In Europe in the Middle Ages, egg whites were used to decorate parchments with gold leaves. In the 1700s, the first glue factory was founded in Holland, which manufactured hide

glue. Later, in the 1750s, the British introduced fish glue. As modernization continued, new patents were issued using rubber, bones, starch, fish, and casein. Modern adhesives have improved flexibility, toughness, curing rate, and temperature and chemical resistance [2].

Otto Bayer [3,4] developed polyurethanes (PURs) in 1937. In modern times this product turned out to be a fantastic success story, as well as a business of many billions of dollars. PURs are produced by the polyaddition reaction of an isocyanate with a polyol and other low-molecular-weight reagents as chain extenders or cross-linking agents containing two or more reactive groups.

The commercial development of PURs began initially in Germany in the end of the 1930s, with the production of rigid foams, adhesive, and coatings. Owing to the continuous reduction in costs and environmental concern, in the 1990s and the beginning of the present millennium researchers were directed to the substitution of chlorofluorocarbons considered harmful to the layer of terrestrial ozone, so systems have been developed that are free of volatile organic compounds (VOCs), as well as PURs recycling.

PUR can be made in a variety of textures and hardness by varying the particular monomers used and adding other substances. Softer PUR can be made by adding flexible polyethylene glycol segments between urethane links. This strategy is used to make spandex fiber, as well as foam rubber. Careful control of viscoelastic properties can lead to memory foam, which is much softer at skin temperature than at room temperature. PUR foam can be produced by adding a small amount of water to one of the liquid precursors of PUR before they are mixed together. This modifies the polymerization reaction, causing carbon dioxide to be released as the material cures. Gas is generated throughout the liquid, creating relatively uniform bubbles that then harden to form solid foam as polymerization progress. The small proportion of reactions affected by the water result in urea linkages, −NC(O)N−, rather than urethane linkages, so the resulting material should technically be called PUR–co–urea.

In light of this, water-borne systems are gaining importance. These materials find a special application as binders for paints and coating formulations [5,6].

PURs are good adhesives for a number of reasons [7–13].

- They effectively wet the surface of most substrates.
- They can interact with the substrate through polar interactions (e.g., hydrogen bonding).
- They can form covalent bonds with substrates that have active hydrogen atoms (for reactive adhesives).
- Their relatively low molecular weight/small molecular size allows them to permeate porous substrates (for reactive adhesives).
- Through molecular composition the adhesive stiffness, elasticity, and cross-linking can be tailored to suit specific needs.

PUR dispersions have become commercially available since the 1960s. Owing to their significance in industry as well as their academic interest, more than 1,000 patents have been filed over the past 5 decades and these have been reviewed and documented.

Recent patents have mainly focused on the modification of aqueous PUR dispersions for specific end uses [14–18].

Among the water-borne polymer family, PUR dispersions benefited over the past few years from a continuously growing attention by a market that recognizes their high performance and strong potential from soft and rubber properties to rigid thermoplastic or, after curing, to thermoset materials [19].

11.1.1 Polyurethane-Based Adhesives

11.1.1.1 Structure and Raw Materials for Polyurethane-Based Adhesives

One can derive from the patent sources [20–29] which raw materials may be selected for the formulation of PUR-based pressure-sensitive adhesives (PSAs). They are as follows.

- Diisocyanates (aliphatic, aromatic, cycloaliphatic)
- Diols or polyols
- Carboxylic acid-containing hydroxylic groups
- Resin
- Accelerator
- Wetting agent

11.1.1.1.1 Isocyanates

Organic multifunctional isocyanates, usually with two or three isocyanate groups in the molecule, are compounds in which the isocyanate group, −NCO, is attached to an organic group. The reactivity of the highly unsaturated isocyanate group led to its study and use in a great variety of reactions. Multifunctional isocyanates have been particularly useful for the systematic build-up of polymer molecules with tailored properties.

The most widely used isocyanates are the 2,4 and 2,6 isomers of toluene diisocyanate (TDI). The manufacture of TDI involves the dinitration of toluene, followed by catalytic hydrogenation to diamine and phosgenation. TDI is a colorless liquid with a boiling point of 120°C at 100 mm Hg.

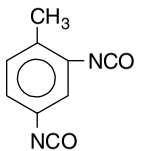
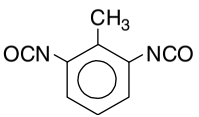
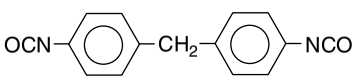
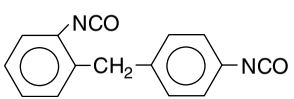
4,4'-Diphenylomethane diisocyanate (MDI) is another important raw material in PUR manufacture. It is a solid at 37°C and has a tendency to dimerize at room temperature.

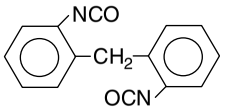
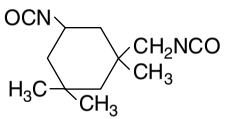
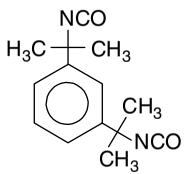
PUR polymers based on aromatic isocyanates tend to yellow upon prolonged exposure to sunlight. Beachell and Ngoc Son demonstrated that the color could be the result of oxidation of preexisting amino end-groups and further oxidation of amines liberated during thermal degradation at 150–215°C to form products such as polypseudourea ether and a still-unknown material derived from TDI.

The first commercial aliphatic diisocyanate to be available was 1,6-hexamethylene diisocyanate (HDI). It is less reactive than either TDI or MDI, but in the presence of a catalyst the rate of reaction is enhanced.

Several isocyanate types are available in the market (Table 11.1).

TABLE 11.1 Commercial Isocyanates

Common Name/CAS Name	Formula	Structure	Molecular Weight	MP (°C)	BP (°C)	Density (g/l)
Toluene 2,4diisocyanate (TDI)/ 2,4-diisocyanato-1methylbenzene	$C_9H_6O_2N_2$		174.2	21.8	121 (10 mm Hg)	1.061 (20°C)
Toluene 2,6diisocyanate (TDI)/ 2,6-diisocyanato-1methylbenzene	$C_9H_6O_2N_2$		172.2	18.2	120 (10 mm Hg)	1.2271 (20°C)
65:35 mixture of toluene 2,4- and 2,6-diisocyanate (TDI65/35)	$C_9H_6O_2N_2$		174.2	5.0	121 (10 mm Hg)	1.222 (20°C)
80:320 mixture of toluene 2,4- and 2,6-diisocyanate (TDI80/20)	$C_9H_6O_2N_2$		174.2	13.6	121 (10 mm Hg)	1.221 (20°C)
4,4'-Diphenyl methane diisocyanate (MDI)/1.1'methylene-bis (4isocyanatobenzene)	$C_{15}H_{10}O_2N_2$		250.3	39.5	208 (10 mm Hg)	1.183 (50°C)
2,4-Diphenyl methane diisocyanate (MDI)/1-isocyanato2-(4-isocyanatophenyl) methylbenzene	$C_{15}H_{10}O_2N_2$		250.3	34.5	154 (1.3 mm Hg)	1.192 (40°C)

2,2'-Diphenyl methane diisocyanate (MDI)/1,1'-methylene-bis (2-isocyanatobenzene)	$C_{15}H_{10}O_2N_2$		250.3	46.5	145 (1.3 mm Hg)	1.188 (50°C)
Hexamethylene diisocyanate (HDI)/1,6-diisocyanatohexane	$C_8H_{12}O_2N_2$	$OCN\text{-}(CH_2)_6\text{-}NCO$	168.2	−67	127 (10 mm Hg)	1.047 (20°C)
Isophorone diisocyanate (IPDI)/ 5-isocyanato-1(isocyanatomethe) 1,3,3-trimethylcyclohexane	$C_{12}H_{18}O_2N_2$		222.3	−60	158 (10 mm Hg)	1.062 (20°C)
m-Tetramethylxylene diisocyanate (*m*-TMXDI)/1,3-bis(1-isicyanato-1-metylethe) benzene	$C_{14}H_{16}O_2N_2$		244.3	–	150 (50 mm Hg)	1.05 (20°C)

11.1.1.1.2 Polyols

Polyols are the second basic component beside diisocyanates.These raw materials are multifunctional hydroxy-bearing compounds. Polyols are commercially available in wide range of molecular weights and functionalities. There are two types of polyols, polyether polyester polyols. Polyether polyols are characterized as follows:

Functionality	2 to 4
Structure	Linear, branched, multibranched
OH number	30 to 700

11.1.1.1.3 Additives

Resins

- Hydrocarbon resins
- Modified colophonium
- Polyterpene resins
- Terpene phenol resins
- Indene–cumarone resins
- Ketone resins
- Aldehyde resin
- β-Pirene resin

Accelerator

Preferably Sn (II) octoate

Wetting Agent

The wetting problems during coating that occur as a result of different polar forces can only be improved through the addition of a wetting agent [30].

11.2 Polyurethane-Based Pressure-Sensitive Adhesives

All commercial PSAs are based on polymers, mainly coming from six families: acrylics, natural and synthetic rubber, silicones, PURs, polyesters, and polyethers (Figure 11.1). There are also niche markets for silicone PSAs, where low-temperature use or high-temperature stability is required and cost is not an issue.

PUR PSAs are less well known because their applications thus far have been limited to low-tack and low-peel adhesive protective films. Environmental reasons are the cause for the increase in research, development, and production of water-borne systems, particularly those based on PURs [31–33].

The raw materials for PUR-based PSAs and their use for special tapes were described by Benedek [34]. PUR-based thermoplastic elastomers were discussed in Ref. [35]. PUR dispersions and functionalized PURs for PSAs were described by Benedek in Ref. [36].

11.2.1 Monomers

For PUR-based PSAs we used diisocyanates, polyols, hydroxyterminated polybutadiene, dihydroxy acids, or their derivatives.

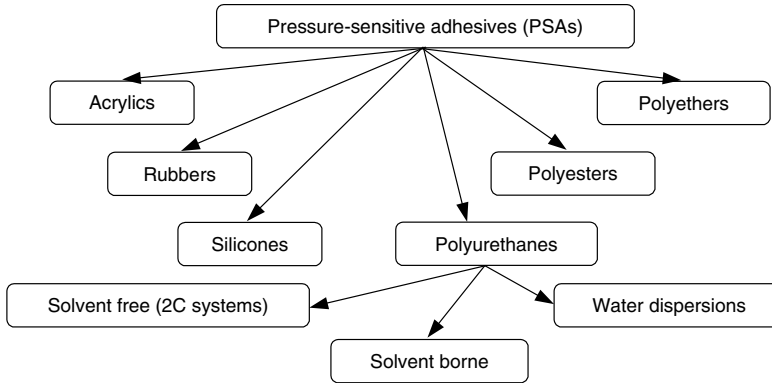


FIGURE 11.1 Kinds of PSAs.

TABLE 11.2 Monomers in the PUR Polymer Chain

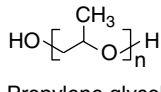
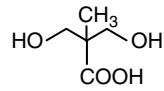
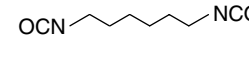
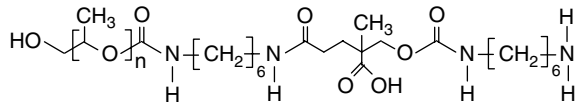
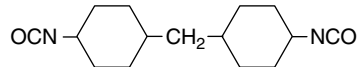
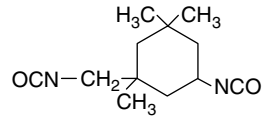
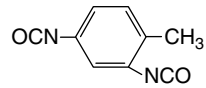
PUR Dispersion		
HO–X–OH	HO–Z–OH	OCN–Y–NCO
		
Propylene glycol	Carboxylic acid DMPA	HDI
HO–X–OH OCN–Y–NCO HO–Z–OH OCN–Y–NCO		
		
Polyurethane polymer chain		

Table 11.2 demonstrates the formula of some monomers with their place in the PUR chain. The basic chemical components of water-borne PURs are all building blocks that are known from solvent-borne PURs. Mainly, they are diisocyanates, polyols, amines, catalysts, and additives [37–40].

A number of reactions in the preparation process are important. The polyaddition reaction of isocyanates with polyols leads to PUR polymers. In a second reaction, the remaining isocyanate groups react with amines to form ureas. The third reaction between isocyanate and water comes into play. The isocyanate group is hydrolyzed to yield amines and ureas are formed. Urea groups are desired in the formed PUR because they contribute to a major extent to the typical properties of high-performance water-borne PURs.

TABLE 11.3 Diisocyanates That Increase Adhesion in PUR Adhesives

Formula	Structure	Melting Temperature (°C)
HMDI		60–71
IPDI		About −60
TDI		About −80

The isocyanates are very important to the introduction of urethane groups into the polymer. Depending on their structure, the final properties of the polymer are influenced. Mostly aliphatic diisocyanates, like the linear HDI and cycloaliphatic dicyclohexylmethane (H_{12}MDI) and isophorone diisocyanate are used. The aromatic TDI and diphenylmethane diisocyanate are more difficult to handle as a result of their high reactivity to water. Some of the newer production processes allow them to be built in. Diisocyanates increase adhesion in PUR adhesives (Table 11.3).

Hydroxyterminated polybutadiene (HTPB) is generally used in the preparation of adhesives, coatings, and elastomers and in many areas such as the automobile, coatings and paints, building-trade, electronics, and medicine fields [41–44].

When the soft segments in PUR chains are formed by an oligobutadiene, instead of a polyether or polyester, high segregation between the hard and soft domains occurs due to the polar character of the oligobutadiene chain [45].

As a consequence, some striking features, such as high resistance to acid or base hydrolysis, the ability to retain elastomeric behavior at low temperatures, low water permeability, and improved mechanical properties [46], have been developed. The presence of HTPB in PUR chains brings important characteristics to the final product.

11.2.2 Other Components

11.2.2.1 Tackifiers

The formulator's approach to a PSA is to blend elastomers, tackifiers, plasticizers, and other additives to achieve the properties needed. The elastomers contributes cohesive strength, a flat rubbery plateau, and low T_g. The tackifier, that is, a solid, glassy, low-molecular-weight plasticizer that is soluble in the elastomer, increases the T_g of the

elastomer/tackifier blend while simultaneously decreasing room temperature modulus and increasing tack. The effect of a tackfier is to increase the resulting T_g of the soluble blend of the elastomer and the resin and to reduce the modulus at room temperature to improve tack. It may, however, cause the modulus to drop excessively at higher temperatures, reducing shear strength.

11.2.2.2 Plasticizers

Plasticizers of the PUR PSA can be accomplished using low-molecular-weight plasticizers. These materials lower at all temperatures; however, these plasticizers may be too volatile or water soluble to remain permanently in some PSA applications. These materials can, however, be used in small amounts as coalescing agents to accelerate film formation so as to speed up the development of the final PUR properties. The modulus is lowered at all temperatures above the plasticizer T_g and the flatness of the rubbery plateau is improved at this level of addition. The plasticizer level alone is not sufficient to achieve tack at ambient temperatures. By blending both tackifiers and plasticizers, we can lower the modulus to achieve tack, as will be demonstrated later.

11.2.3 Water-Based Polyurethane Pressure-Sensitive Adhesives

Some 15 years ago, water-borne PURs, or PUR dispersions, started gaining importance. Environmental and legislative pressures have driven the industry to concentrate on water-borne polymers. PUR dispersions have experienced an upsurge in importance over the past few years. A number of interesting applications have been a major reason for this upsurge. Aqueous PUR dispersions fall into two major classes.

1. Aqueous polymer dispersions prepared by emulsion polymerization
2. Dispersions of preformed polymers in water

Depending on the starting components, solvents, and the process sequence, several preparation methods are common, including, most importantly, the following.

1. Acetone process
2. Melt-dispersion process
3. Prepolymer mixing process
4. Ketamine–ketazine process
5. Other processes

The first step common to all these processes is the conventional synthesis of PUR, in which diol or polyols are reacted with diisocyanates. In a second step, the prepolymer chain is extended and dispersed in water in different ways by introducing hydrophilizing solubilizing groups. If we want to achieve low viscosity in the system, we must use one of the following methods.

- If the urethane polymer is of low molecular weight, a chain-extension step is required at the aqueous dispersion stage to achieve the necessary high molecular weight (e.g., prepolymer mixing process or ketamine–ketazine process).

- We must use the urethane polymer heat to facilitate dispersion in water (the melt dispersion process).
- We must the urethane polymer dissolve in a solvent and the solvent remove after the aqueous dispersion step (the acetone process).

In the acetone process, chain extension of the hydrophilic isocyanate prepolymer with diamines is performed in a solvent (e.g., acetone) to yield PUR polyureas. High reproducibility is possible because polymer formation is accomplished in a homogeneous solution. Through the addition of water and the removal of the solvent, a purely water-borne dispersion of small particle size is formed. The aqueous dispersion is generated by precipitation of the hydrophobic segments and the phase inversion of an intermediately generated inverse emulsion.

The acetone process allows the production of PUR dispersions with smaller particle size and a more narrow particle size distribution.

In the melt dispersion process an ionically or nonionically modified isocyanate modified isocyanate-terminated prepolymer in the form of a low-viscosity solution is reacted with urea or ammonia to form a capped oligomer with terminal biuret groups. In the next step, in the water, chain extension is accomplished by methylation of the biuret groups with formaldehyde and reduction of the pH to initiate polycondensation reactions.

In the prepolymer mixing process a hydrophilically modified polymer with free isocyanate groups is mixed with water. Chain extension with amines in the aqueous phase is then accomplished. We could also add a prepolymer to the water (inverse process). This process is a common method used to produce PUR dispersions.

In the ketamine–ketazine process, blocked amine or hydrazine is blended with the isocyanate prepolymer and dispersed in the aqueous phase. In the next step, the amino function is liberated simultaneously by hydrolysis and chain extension occurs. The liberated amine is already homogeneously distributed in the dispersed particles.

Many variations of these processes exist. For example, a special process for the production of water-borne polymer dispersions is the radical polymerization of unsaturated building blocks containing urethane groups with acrylate, methacrylate, or other monomers.

11.2.3.1 General Considerations

PURs are a class of adhesive raw materials that over the past 50 years have developed a reputation for reliability and high performance in many applications, including the footwear industry, furniture assembly, and the automotive industry. PUR adhesives are particularly known for forming bonds with excellent strength, plasticizer resistance, and durability. As environmental legislation limits the further use of solvent-based systems, there has been a rapid growth in the area of water-based PURs.

Reasons for the increasing trend to solvent free adhesives systems include the following.

1. Ecological aspects
   - Superior working hygiene during handling
   - Higher working safety during handling
   - Health precautions for the end product

2. Economical aspect
   - Lower investment costs (solvent recovery or incineration and explosion protection not necessary)
   - High solids content
   - Positive image effects [47]

Generally, PUR adhesives can be cross-linked chemically or by radiation. Conventional cross-linkable, thermal cross-linkable, and ultraviolet (UV)-cross-linkable PUR formulations exist. The UV cross-linking of various photoreactive PUR coatings is based on the photoinitiation of free radical cross-linking reactions.

11.2.3.2 Cross-Linking of Water-Based Polyurethane Pressure-Sensitive Adhesives

UV-cross-linkable PUR PSA dispersions benefited over the past few years from a continuously growing attention by a market that recognizes their excellent versatile performance. The chemistry and the synthesis process of water-borne PUR PSAs is illustrated in Figure 11.3.

11.2.3.2.1 Chemical Cross-Linking

Pure PUR polymer in water normally demonstrates lower levels of tack and peel adhesion (adhesion). Tackification of the PUR systems is very complex; it increases tack and peel resistance, but reduces cohesion. Aging of the tackifier may cause brown spots or overall yellowing of the dispersion adhesive. However, because water is much less expensive than solvents and the solids content of water-based PURs is higher, they are more economical in use, which is important in the competitive paper label and packaging tape markets. Applications are usually limited to indoor use because the water resistance of these adhesives is limited, although improvements are being made continuously [48].

Cross-Linking with Multifunctional Polyisocyanates Polyisocyanate cross-linkers will improve the performance of PUR dispersions through cross-linking reactions that occur at room temperature in the adhesive film as the adhesives cures to full strength. The use of multifunctional polyisocyanates as curing agents for acrylics was discussed by Czech in [49].

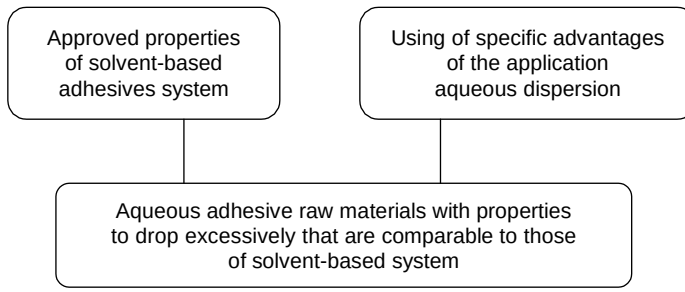


FIGURE 11.2 Target for the development of aqueous adhesive raw materials.

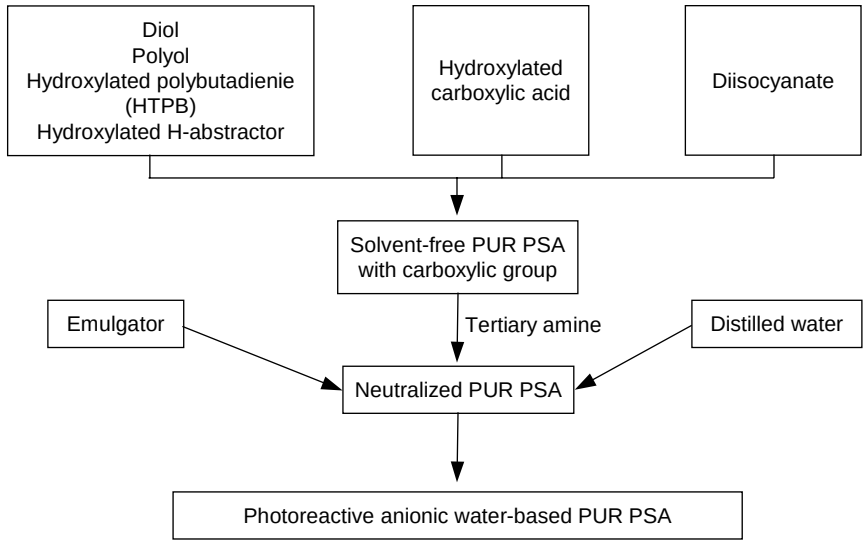


FIGURE 11.3 Synthesis of water-borne photoreactive PUR self-adhesives.

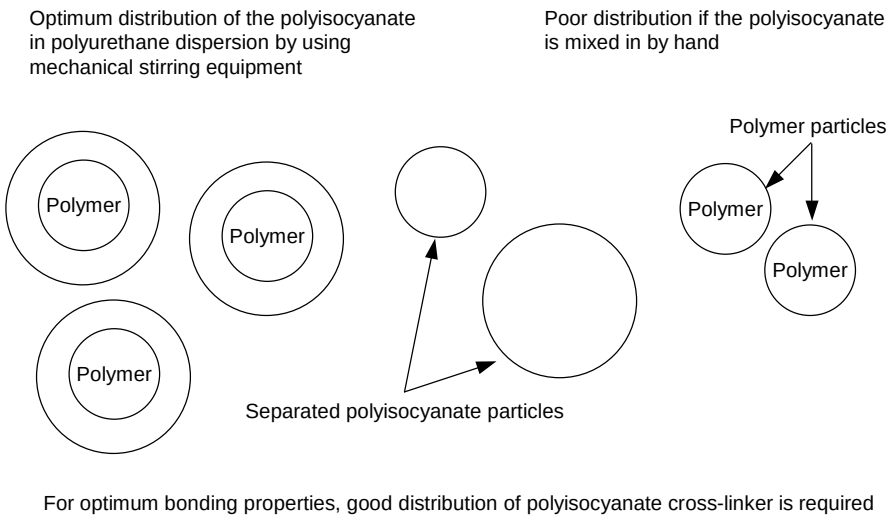


FIGURE 11.4 Optimum distribution of the polyisocyanate [50].

Polyisocyanate cross-linkers are recommended to be used at a level of 2–5% based on the dispersion. The level used for typical laboratory testing with PUR dispersions is 3% based on the wet weight of a dispersion containing 40–50% solids. The polyisocyanates are dispersed in the aqueous polymer with rapid stirring (Figure 11.4). Depending on the shear force applied, the particle size of the dispersed polyisocyanate varies. To improve the dispersibility of an isocyanate, it may be diluted with an organic solvent, for

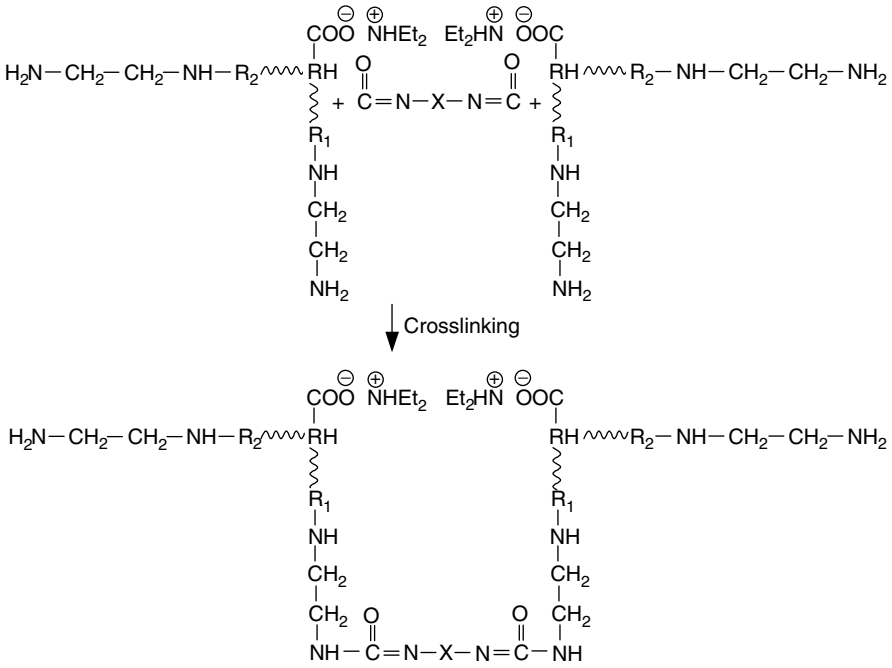


FIGURE 11.5 Cross-linking of water-borne PUR PSAs using multifunctional isocyanates.

example, propylene carbonate, to reduce the viscosity. Water-dispersible polyisocyanates have been developed that contain a higher internal emulsifier level and thus allow easier dispersion in water [50].

Solventless multifunctional isocyanate cross-linkers are available based on cycloaliphatic, aliphatic, aromatic, or heterocyclic diisocyanates that can be dispersed into a water-borne PUR formulation. Aliphatic versions are preferred for non-yellowing coatings. Multifunctional isocyanates undergo the normal reactions with active hydrogen atoms of amino groups of the PUR polymer chain in dried coatings (Figure 11.5).

Cross-Linking Using Melamine–Formaldehyde Resins Melamine–formaldehyde resins are an interesting class of cross-linking agents for the diverse polymers for use at higher temperatures in thermoset coatings, including hydroxyl, carboxyl, or amine groups. The use of amino resins as curing agents was discussed by Czech in [51]. The melamine–formaldehyde resins are generally known as amino resins. They enable a controlled cross-linking reaction and accurate adjustment of the required adhesive properties. Melamine–formaldehyde resins are characterized by their reactive end groups. Cross-linking speed is practically zero at room temperatures, whereas it increases exponentially above 100°C. Thus, cross-linking begins after only drying of the PSA.

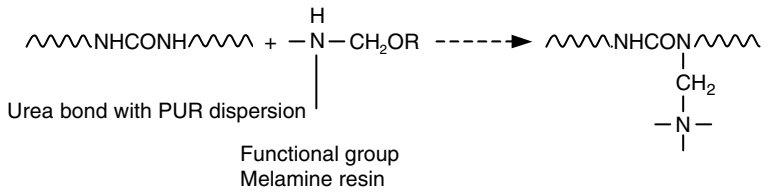


FIGURE 11.6 Scheme of cross-linking reaction of a PUR dispersion with melamine resins.

Amino resins can be used for the cross-linking of water-borne PUR PSA at temperatures between 105 and 150°C. The amino resins containing imino functionality or high methylol are highly reactive, but inclined to self-cross-linking reactions catalyzed by free acid groups distributed on the polymer (Figure 11.6).

11.2.3.2.2 Radiation-Induced Cross-Linking

Over the past 10 years, the number of UV-curing PUR dispersions has been growing. They combine both PUR properties and the fast and economic UV curing step. Although the advantage in productivity used to be the main driving force, an even more increased interest can be observed due to the worldwide efforts limiting emissions of VOCs by legislation. Moreover, UV-cured PSAs are attractive to the industry because they promise a level of performance that is perhaps inaccessible with conventional aqueous and hot-melt products. These improved properties include heat resistance, shear strength, and chemical resistance and are due to the cross-linked nature of the cured film. Such enhanced properties were previously obtainable only through the use of solvent-based products. Many factors, including cure condition, chemical composition, and physical dimensions (i.e., thickness), influence the performance properties of UV-curable PSAs [52–57].

The balance between cohesive and adhesive strengths within the cross-linked coatings is very important for the performance of UV PSA. The combination of different UV cross-linkable adhesives allows the manufacturing of films with zones with different cohesion/adhesion properties and offers novel chances to develop innovative tapes with new unique features [58–60]. The ratio of tack, adhesion, and cohesion with UV cross-linkable PUR PSAs can be varied within wide limits by controlling the amounts of radiant energy applied to the adhesive film after it has been coated.

As described in Ref. [61], that pass through a "curing window" within the same range of UV doses. The curing window represents optimum conditions for curing. To reach optimal pressure-sensitive performance with UV cross-linkable adhesives, it is necessary to find process settings that lead to balanced values of tack, peel adhesion, and shear strength for the preferred application. Considering that a UV-cured PSA coating exhibits good adhesion and medium cohesion, and a good-cross-linked good cohesion and medium adhesion [62].

The components of PSA systems (of course, those that are not chemically linked) can migrate onto the surface of the finished coating. This phenomenon is called chalking

or bleeding and the migrating components are pigments, plasticizers, conventional photoinitiators, or fillers and by-products of photoinitiators after UV exposure. Only a fraction of the photolytically generated radicals become part of the polymer network, and the initiator molecules do not react completely [63,64].

The UV-light-induced cross-linking technique calls for the use of a photoinitiator. This element is therefore one of the key components in UV cross-linking. The outcome of such a polymerization is highly dependent on the choice of photoinitiator, its chemical nature, and the concentration used [65]. UV cross-linkable PUR PSA systems must start the radical cross-linking reaction by hydroxylated conventional hydrogen abstractor initiators or multifunctional H-abstractors. Photoinitiators for UV curing were discussed by Czech in Ref. [66], and by Benedek in Ref. [67]; the principles of photocuring, photoinitiators, techniques of UV-induced polymerization, and properties of UV-curable PSAs were discussed in detail by Do and Kim in [68].

The photoinitiators in the second class undergo a primary process of hydrogen atom abstraction from the environment (R-H), which may be the resin itself or a solvent, to produce a ketyl radical. The photoreductive ability of the environment is an important factor. It is related to the carbon–hydrogen bond strength of the species donating the hydrogen atom. The type II photoinitiators produce radicals via intermolecular hydrogen abstraction. These photoinitiators demand thiols or alcohols for the generation of radicals that are efficient in initiating cross-linking. These photoinitiators also need hydrogen donors, such as amines. The intermolecular H-abstraction photoinitiators include special benzophenone and its derivatives such as benzil, quinines, xanthone, or thioxanthone [69]. Figure 11.7 illustrates the build-up of type II photoinitiators.

These groups of multifunctional H-abstractors represent saturated photoinitiators that contain at least two photoreactive structures in the molecule and form cross-links with the polymer chain of the PSAs by UV radiation [70]. It is possible to synthesize so-called migration-free photoinitiators by specific constructions (e.g., from xanthones, thioxanthones, multifunctional benzophenones, fluorenones, or benzyls) (Figure 11.8).

Regarding their chemical structure, we could use multifunctional photoinitiators with common UV sources due to their different UV characteristics. Incorporating multifunctional photoinitiator type II into the backbone of the PUR PSA polymer allows their cross-linking with UV radiation. Further, incorporation of multifunctional H-abstractor photoinitiators into the PUR polymer chain increases the efficiency of cross-linking obtainable by inclusion of the photoinitiator monomer in the adhesive. Thus, only small amounts of multifunctional hydrogen abstractors are needed to achieve useful degrees of cross-linking. PUR polymer structures that cross-link directly under the influence of UV energy require special photosensitive groups from an incorporated hydrogen abstractor network formation (Figure 11.9).

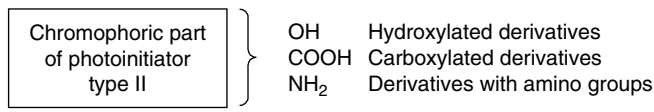


FIGURE 11.7 General examples for suitable H-abstractor photoinitiators.

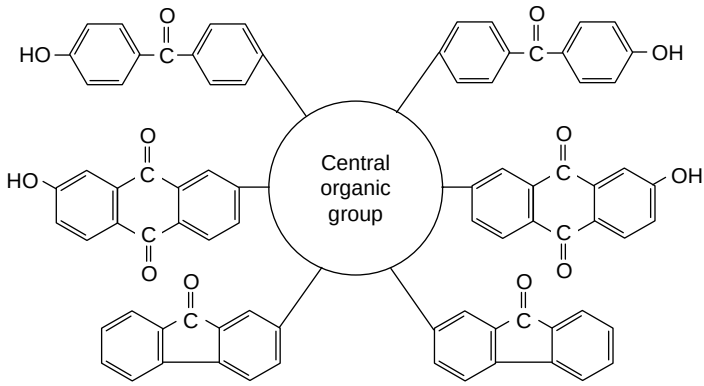


FIGURE 11.8 Multifunctional hydrogen abstractor photoinitiators.

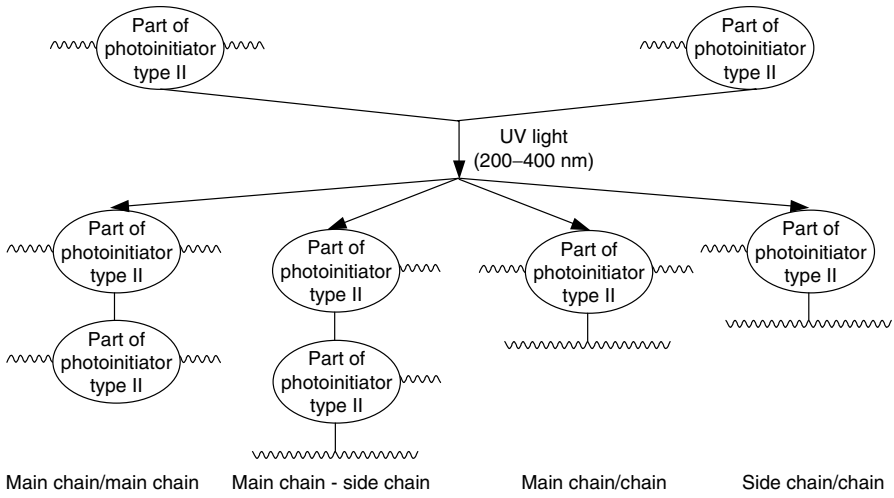


FIGURE 11.9 PUR photocross-linking by using of the H-abstractor photoinitiators incorporated into the polymer chain.

11.3 Nonisocyanate Polyurethanes

Nonisocyanate PURs [71] (NIPUs) are a group of new, innovative backbone polymers that exhibit potential for applications in PSAs. Nonisocyanates are employed for their formation, as the chemical name suggests at first glance. Instead, such compounds are formed as a result of the reaction of cyclocarbonates with polyamines (Figure 11.10).

Urethane diol type compounds and their functional modifications offer potential as backbone polymers for PSAs. They feature some advantageous properties, such as insensitivity to humidity, stability to hydrolysis, and improved chemical as well as temperature resistance. NIPU class products may be modified by several reactive groups. For employment in PSA formulations, methacrylates and other unsaturated groups are

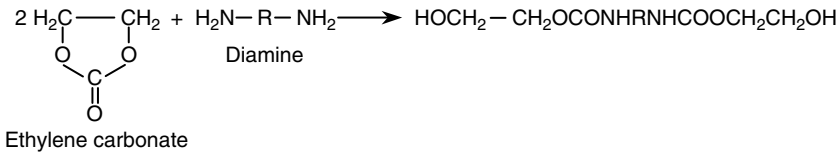


FIGURE 11.10 Synthesis of urethane diol.

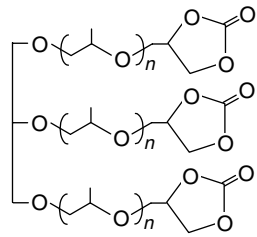


FIGURE 11.11 Cyclocarbonate of Heloxy 84 where $n = 8$.

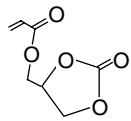


FIGURE 11.12 Propylene carbonate acrylate.

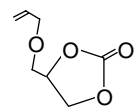


FIGURE 11.13 Glycerol carbonate vinyl ether.

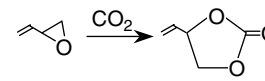


FIGURE 11.14 Synthesis of vinyl ethylene carbonate from epoxybutene.

preferred for modification purposes because such types of moieties offer broad potential for radiation curing. NIPUs experienced their decisive breakthrough when economically feasible methods for the synthesis of cyclocarbonates became accessible because these compounds are the chemical basis for NIPU formation (Figure 11.11).

Cyclocarbonates may be synthesized according to different methods. The selection of raw materials determines the product properties. A group of oligomeric cyclocarbonates can be formed in an economically feasible manner by bubbling carbon dioxide through a liquid monomer or oligomer product in the presence of a suitable catalyst. Thus, multialkylene carbonates are obtained from epoxy compounds by reacting Heloxy Modifier 84 (Hexion) with CO_2. Heloxy is a trifunctional polyoxypropylene with terminal epoxy groups, which reacts with 3 mol of CO_2 forming trifunctional multialkylene carbonates.

Typical cyclocarbonates with unsaturated moieties are as follows.

- Propylene carbonates (methacrylate) (Figure 11.12)
- Vinyl carbonates
- Glycerol carbonate vinyl ethers (Figure 11.13)
- Vinyl ethylene carbonates (Figure 11.14)

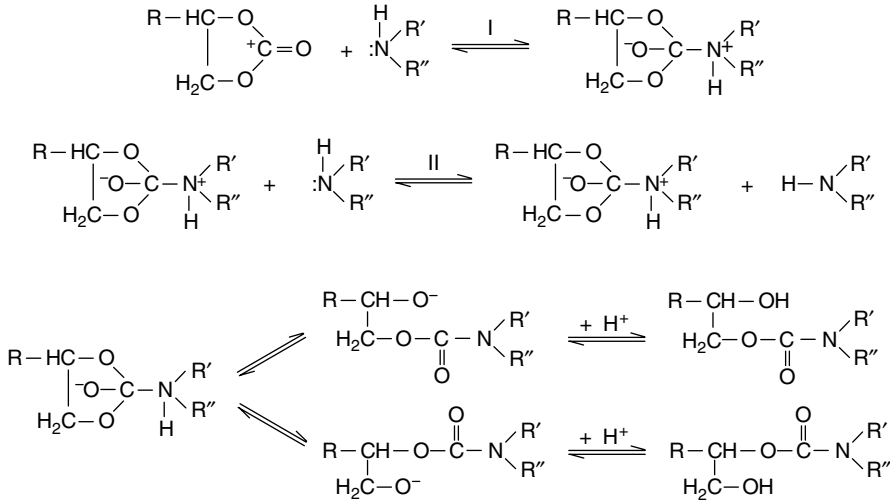


FIGURE 11.15 Reaction of cyclocarbonates with amine compounds.

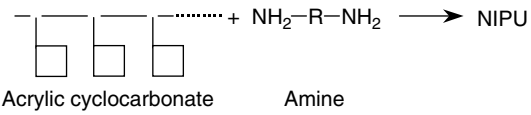


FIGURE 11.16 Curing process of acrylic NIPU.

The examples in Figure 11.15 demonstrate the reaction of cyclocarbonates with amine compounds.

Cross-linking reactions of NIPUs modified with acrylic groups are demonstrate in Figure 11.16. NIPUs offer particular potential as backbone polymers in hot-melt PSAs (HMPSAs). To improve tack and permanent adhesion, such polymers must be modified by suitable tackifier resins and other additives. Such formulations imply interesting innovation potential for new groups of PSA materials for their production as well as for processing and end-use applications (e.g., improved hygienic properties).

11.4 Outlook

PUR dispersions are, at present, predominantly used in the furniture, automotive, and shoe industries. Generally, PUR dispersions are used wherever high initial and final bond strengths, heat resistance, and resistance to moisture and plasticisers are required.

PUR adhesives are used to produce polyvinyl chloride (PVC) membrane-pressed panels for furniture. These adhesives must be used with an isocyanate hardener to

provide the cured adhesive bond and improved high-temperature resistance. The adhesive is sprayed into the profiled surfaces and edges of the medium-density fiberboard (MDF) panels and allowed to dry. During the pressing cycle, the PVC flows into the machined grooves in the panels and around their edges under the dual influence of heat and pressure. The heat also reactivates the adhesive, allowing a bond to form between the PVC and MDF. Panels produced in this way have become very popular for kitchen furniture, and their use in bedrooms and bathrooms is growing [72].

In the automotive industry we used PUR adhesives for laminating interior trim parts. In the United States, about a quarter of new cars currently use a PUR top coat, primarily for high-end models. With the changing attitudes of today's car-buying customers, who increasingly demand better performance, such as excellent surface appearance and acid rain etching protection for their purchases, more American models will certainly use PUR top coats in near future [41].

Currently, a great interest in the development of aqueous PUR dispersion has emerged in the footwear industry because of their lack of flammability and toxicity that comply with restricted environmental legislation (Directive 99/13/EC) with respect to the emission of organic solvents into the atmosphere [73].

PURs are commonly used in a number of medical applications, including catheter and general-purpose tubing, hospital bedding, surgical drapes, wound dressings, and a variety of injection molded devices. Their most common use is in short-term implants.

PUR use in medical applications is appropriate for a variety of applications where the following advantages are needed.

- Cost effectiveness
- Longevity
- Toughness
- High stress/strain

PUR PSAs are also used in medical pads and medical electrodes.

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Appendix: Abbreviations and Acronyms

1. Compounds

AA	acrylic acid
ABC	acrylic block copolymer
ABS	acrylonitrile–butadiene–styrene
AC	acrylic
AHM	acrylic block copolymer-based hot melt
AMA	alkyl methacrylate
AMPS	2-acrylamido-2-methylpropane sulfonic acid
APO	amorphous polyolefin
ATBC	acetyltributyl citrate
ATEC	acetyltriethyl citrate
BA/AA	butyl acrylate–acrylic acid
BAEMA	butyl aminoethyl methacrylate
BA-*co*-MMA-*g*-S	butyl acrylate-methyl methacrylate copolymer with grafted styrene
BA-*co*-MMA-*co*-S	butyl acrylate-methyl methacrylate-styrene copolymer
BNR	butadiene–nitrile rubber
BPO	benzoyl peroxide
BR	butyl rubber
CMC	carboxymethyl cellulose or critical micelle concentration
CPP	cast polypropylene
CSBR	carboxylated butadiene rubber
CTA	chain transfer agent
DACP	diacetone alcohol/xylene cloud point
DBP	dibutyl phthalate
DCPD	dicyclopentadienyl

DDM	dodecyl mercaptan
DMAEMA	dimethylaminoethyl methacrylate
DOP	dioctyl phthalate
EAA	ethylene–acrylic acid
EBA	ethylene–butyl acrylate
EHA	ethylhexyl acrylate
EHA/AA	ethylhexyl acrylate/acrylic acid
EMAA	ethylene–maleic anhydride
EO	ethylene oxide
EPDM	ethylene–propylene–diene multipolymer
EPR	ethylene propylene rubber
EPVC	emulsion PVC
EVAc	ethylene–vinyl acetate copolymer
EVOH	poly(vinyl alcohol), copolymer
GMA	glycidyl methacrylate
HC	hydrocarbon
HDI	hexamethylene diisocyanate
HDPE	high-density polyethylene
HEA	hydroxyethyl acrylate
HEC	hydroxyethyl cellulose
HFBA	heptafluorobutyl acrylate
HLB	hydrophilic–lipophilic balance
HMDI	hexamethylene diisocyanate
H_{12}MDI	cycloaliphatic dicyclohexyl methane
HMPSA	hot-melt pressure-sensitive adhesive
HIPS	high-impact polystyrene
HPC	hydroxypropyl cellulose
HRA	high-release additive
HTPB	hydroxyterminated polybutadiene
IB	isobutene
IBMA	isobutoxy methacrylamide
IOA	iso-octyl acrylate
IPDI	isophorone diisocyanate
IP	isoprene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
M14	sodium tetradecyl 3-sulfopropyl maleate
MAA	methacrylic acid
MAGME	methyl acrylamido glycolate methyl ether
MAM	MMA–BA–MMA block copolymer
MDI	4,4'-diphenylomethane diisocyanate
MDPE	medium-density polyethylene
MeP	methyl pentene
MMA	methyl methacrylate
MMAP	methylcyclohexanone/aniline (cloud point test)

MMT	montmorrilonite
Na-MMT	sodium montmorillonite
NIPU	non-isocyanate polyurethanes
NMA	N-methylol acrylamide
NR	natural rubber
NRL	natural rubber latex
NVCL	N-vinyl caprolactam
NVP	N-vinyl pyrrolidone
OMS	odorless mineral spirit
OPP	oriented polypropylene
OPS	oriented polystyrene
P	plasticizer
PA	polyamide
PAA	poly(acrylic acid)
PB	polybutene
PDFA	pentadecafluoro octyl acrylate
PDMAEMA-*co*-MMA-*co*-BMA	poly(N-dimethylaminoethyl methacrylate-*co*-methyl methacrylate-*co*-butyl methacrylate)
PDMS	poly(dimethyl siloxane)
PE	polyethylene
PEG	polyethylene glycol
PEO	polyethylenoxide
PET	polyethylene terephthalate
PEU	polyester-urethane
PFO	phenol formaldehyde oligomer
PI	polyisoprene or polyimide
PIB	polyisobutylene
PMA-*co*-MVE	poly(maleic acid-*co*-methyl vinyl ether)
PMAA-*co*-EA	poly(methacrylic acid-*co*-ethyl acrylate)
PMAA-*co*-MMA	poly(methacrylic acid-*co*-methyl methacrylate)
PMMA	poly(methyl methacrylate)
PMS	para-methyl styrene
PO	propylene oxide
polyHEMA	poly(2-hydroxyethyl methacrylate)
PP	polypropylene
PS	polystyrene
Pst	polystyrene
PTFE	polytetrafluoroethylene
PUR	polyurethane
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
PVDF	poly(vinylidene fluoride)
PVE	polyvinyl ether
PVOH	poly(vinyl alcohol)
PVP	polyvinyl pyrrolidone

RR	rubber–resin
RSH	thiol
SA	succinic acid
SAN	styrene–acrylnitryl
SB	star-branched (polymer)
SBC	styrene block copolymers
SBR	styrene–butadiene–rubber
SBS	styrene–butadiene–styrene
SDED	sodium dodecyl diphenyl ether disulfonate
SDPS	sodium dodecyl phenyl sulfonate
SDS	sodium dodecyl sulfate
SEB	styrene–ethylene–butene
SEP	styrene–ethylene–propylene
SHM	styrenic hot-melt pressure-sensitive adhesive
SI	styrene–isoprene
SIBS	styrene-isoprene–butadiene-styrene
SIS	styrene–isoprene–styrene
SPVC	suspension polyvinyl chloride
T	tackifier
TBC	tributyl citrate
TDI	toluene diisocyanate
TEC	triethyl citrate
TMAEMA	N-trimethylammonium ethyl methacrylate chloride
TPE	thermoplastic elastomers
TPU	thermoplastic polyurethane
TRIS	trimethylolpropane mercaptopropionate
VAc	vinyl acetate
VC	vinyl chloride
Vi	vinyl
VLDPE	very-low-density polyethylene
VP	4-vinylpyridine

2. Terms

AFERA	Association of European Tape Manufacturers
AFM	atomic force microscopy
ASE	alkali-soluble emulsions
ASTM	American Society for Testing and Materials
ATR-FTIR	attenuated total reflectance/Fourier transform infrared
ATRP	atom transfer radical polymerization
BGVV	Bundes Gesundheitsamt (German Sanitary Administration, formerly BGA)

BOPP	bi-axially oriented polypropylene
bp	boiling point
BUR	blow-up ratio
CD	cross-direction
CEN	European Committee for Standardization
CLC	carcass-like cross-linker, carcass-like complex
COF	coefficient of friction
Cw	coating weight
Cw_{cr}	critical coating weight
Da	Dalton
DCI	direct charge imaging
DDI	dart drop impact
DIN	Deutsche Industrie Norm (German Industrial Standard)
DMA	dynamic mechanical analysis
DMTA	differential mechanical thermal analysis
DPI	dots per inch
DSC	differential scanning calorimetry
DZ	diffusion zone
E	modulus of elasticity, bond energy
EB	electron beam
EPA	Environmental Protection Agency
ΔE	bonding energy
F	force
FDA	Federal Drug Administration (USA)
FFP	film-forming polymer
FTIR	Fourier transform infrared
ΔF	free energy of complex formation
G′	storage modulus
G″	loss modulus
G_n^o	plateau modulus
GARField	gradient at right angles to the field
GMP	Good Manufacturing Practices
GPC	gel permeation chromatography
HS	hot shear
ΔH	the change in enthalpy relating to the energy of interpolymer bond
IR	infrared
ISO	International Organization for Standardization
KS	Krämer–Sarnow (method)
LBL	layer-by-layer (construction)
LC	liquid crystalline
LCST	lower-critical solution temperatures
LLC	ladder-like cross-linker, ladder-like complex
LT	loop tack

MD	machine direction
M_e	entanglement molecular weight
MFI	melt flow index
MFT	minimum film-forming temperature
MI	melt index
M_n	number average molecular weight
M_w	weight average molecular weight
$MOPP_c$	mono-oriented propylene copolymer
Mp	melting point
MPR	melt-processed rubber
MVTR	moisture vapour transmission rate
MW	molecular weight
MWD	molecular weight distribution
NIR	near infrared
NMR	nuclear magnetic resonance
P	180° peel force
PFG	pulsed field gradient
PN	plasticity number (Williams)
PSA	pressure-sensitive adhesive
PSP	pressure-sensitive product
PSTC	Pressure-Sensitive Tape Council
Q	heat
QSPR	quantitative structure–property relationship
QUV	accelerated weathering tester
R	gas constant
R^2	regression parameter
RB	rolling ball
R&B	ring and ball
RBSP	ring and ball softening point
RC	rolling cylinder
RFID	radiofrequency identification device
RH	relative humidity
RT	room temperature
SAF	self-adhesive film
SAFT	shear adhesion failure temperature
SB	solvent-based, or star-branched
SF	sol fraction
SP	softening point
SR	swell ratio
SS	stainless steel
ΔS	the change in entropy under complex formation
T	temperature
T_{iso}	isotropization point
T_g	glass transition temperature
T_m	melting point

t	time
t^*	durability of adhesive joint
tan δ	phase angle, $\equiv G''/G'$, dissipation factor
TDD	trans-dermal drug delivery
TEM	transmission electron microscopy
TEWL	trans-epidermal water loss
TM	tapping mode
UCST	upper-critical solution temperature
UV	ultraviolet
V_{deb}	debonding rate
VIP	variable image printing
VOC	volatile organic compound
W	work, practical work of adhesion
W_b	work of viscoelastic deformation up to break
WB	water-based
w_i	weight fractions
WLF	William–Landel–Ferry
ZN	Ziegler–Natta
Θ	contact angle
γ	surface energy
σ_b	stress at break, ultimate tensile strength
σ_{max}	maximum debonding stress in probe tack test
σ_n	nominal stress
ε	relative elongation
ε_b	ultimate elongation (tensile strain)

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Material Science

Made up of three stand-alone references, the **Handbook of Pressure-Sensitive Adhesives and Products** offers a complete guide to the fundamentals, manufacturing, and applications of pressure-sensitive adhesives and products. Indispensable and current, these books cover the fundamental processes involved with the design of pressure-sensitive adhesives and products. They discuss the technology and equipment used in their manufacture and explain the theory and practices used to develop assorted products. Each book is packed with state-of-the-art data.

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