

POLYMERS COATINGS

TECHNOLOGY
and APPLICATIONS



Edited by Inamuddin, Rajender Boddula,
Mohd Imran Ahamed, & Abdullah M. Asiri

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Preface

Polymer coatings are thin polymer films that are applied to flat surfaces or irregular objects. Protective and decorative layers can be served by these coatings. They can be used as functional coatings with corrosion inhibitors or for decorative purposes like in paints. Polymeric coatings are known to be made of organic materials. However, they may contain metallic or ceramic grains to enhance endurance, properties or appearance. Polymeric coatings can be obtained using natural and synthetic rubber, urethane, polyvinyl chloride, acrylic, epoxy, silicone, phenolic resins or nitrocellulose, etc. There is a wide range of fabrication methods to design and construct polymer-coated materials. Compared to conventional coatings, they offer efficient and cost-effective coatings, facile fabrication methods with excellent properties such as corrosion, wear, and heat resistance, higher mechanical strength, and additional benefits, including good chemical and blocking resistance, and excellent scratch/abrasion resistance. Besides which, high gloss to matt looks, soft-touch effect, no color change after UV exposure, excellent adhesion on metal and plastics, short drying time, fast hardness development, and easy formulation are other advantages of these coatings. Polymer coatings have various applications in the field of painting, storage media, semiconductors, optical devices, fluorescent devices, etc., and interest in them has increased due to their applications in areas such as electronics, defense, aeronautical and automotive industries.

This edition of *Polymer Coatings: Technology and Applications* explores the cutting-edge technology of polymer coatings. It discusses fundamentals, fabrication strategies, characterization techniques, and allied applications in fields such as corrosion, food, pharmaceutical, biomedical systems and electronics. It also discusses a few new innovative self-healing, antimicrobial and superhydrophobic polymer coatings. Subsequently, current industrial applications and possible potential activities are also discussed. This

book is an invaluable reference guide for engineers, professionals, students and faculty members working in areas such as coatings, polymer chemistry, and materials science and engineering. Based on thematic topics, this edition contains the following eighteen chapters:

Chapter 1 provides an up-to-date account of fabrication methods for polymer coatings from the basic science to the latest innovations. The techniques which are described and discussed include blade coating, dip coating, spray coating, thermal spray coating, pulsed laser deposition, plasma polymerization, flow coating, spin coating, sol-gel and grafting.

Chapter 2 includes the different fabrication methods of organic/inorganic coating, namely, sol-gel method, cold spray technique, chemical vapor deposition, physical vapor deposition, thermal spray coating, electroplating deposition and electroless deposition. The classification of different coating methods for various organic/inorganic matrices and nanofillers are reported in detail.

Chapter 3 describes various eco-friendly dry powder coating techniques explored in the formulation and development of dry powder inhalers. Additionally, the chapter also includes a segment detailing the process analytical technology techniques, force controlling agents, implications in inhaler device coating and use of computational fluid dynamics in coating technology.

Chapter 4 first introduces the growth of bioinspired superhydrophobic coatings. Then, several theoretical backgrounds are discussed briefly. Afterwards, various methods are considered relating to the importance of creating chemical and physical textures on the surface. Additionally, the development of superhydrophobic and self-cleaning coatings with added nanoparticles are also presented.

Chapter 5 first investigates the nature (substrate-substance) and applications of superhydrophobic coatings. Afterwards, superhydrophobic coating applications are divided into three major categories of restrictive attributes, self-cleaning and smart attributes. All applications of hydrophobic coatings which have been examined in several studies are discussed.

Chapter 6 provides a brief overview of adsorptive polymer coatings, their techniques and a comprehensive comparison. Moreover, adsorptive polymer

coating applications in various fields are also discussed. Furthermore, a future perspective of existing challenges provides a better direction and understanding for overcoming these challenges in coming days.

Chapter 7 deals with the formulations and chemistry of polyurethane (PU) coatings, and also provides an insight into the development of PU over the conventional coatings. A detailed discussion of the advantages of PU coatings and their future scope in industry is also presented.

Chapter 8 emphasizes a unique type of polymer coatings based on electroactive material. Fabrication, essential characteristics, and potential applications of electroactive polymer coatings are discussed.

Chapter 9 deals with the importance of conducting polymer coatings in the field of corrosion resistance.

Chapter 10 discusses the main objectives, materials and techniques used for encapsulating food components or coating food surfaces such as fruits and vegetables, meat and meat products, eggs, cheese, nuts, and fried food. Biopolymers including polysaccharides, proteins, and waxes are the main ingredients used for this purpose.

Chapter 11 discusses the scope of biopolymers as edible coating in food products. The chapter emphasizes the various types of raw materials used for preparing edible coating. The role of edible packaging in microbial spoilage, mechanical damage, and consumer acceptance of food is discussed along with its advantages and limitations and selection criteria as edible coating for different varieties of food products.

Chapter 12 addresses the wider aspects of pharmaceutical coatings using different types of polymers and their applications in the development and manufacturing of conventional and modified release drug delivery systems. A historical perspective on pharmaceutical coatings along with their physical attributes and characterization are also discussed, which will guide researchers and pharmaceutical manufacturers to their appropriate selection.

Chapter 13 summarizes the critical characteristics of self-healing polymeric coatings. Progress in existing self-healing coating methods and realistic frameworks of polymeric coatings are presented. Surface self-regeneration

and anti-corrosive protective layer fractures are discussed. Issues related to the transition from laboratories to valid industrial application of these self-healing technologies are addressed.

Chapter 14 describes various methods that have revolutionized the role of this fascinating strategy in biological science especially in biomedical applications, notably infectious therapy, drug delivery system for therapeutic agent and protective layer for implants and biomedical devices. The major focus is given to some key applications which are trendsetting for surface functionalization of implants and biomedical materials.

Chapter 15 describes the role of polymers against various microorganisms such as bacteria, protozoans and fungi. These polymers mimic the action of antimicrobial peptides which are utilized by immune systems of such living organisms to kill the microorganism. The main purpose of antimicrobial coating is to combat antimicrobial resistance and infections.

Chapter 16 discusses in detail the various processes and techniques that are most commonly used for the coating of polymers which protect active pharmaceutical ingredient (API) against environmental hazards and bodily fluids, protecting the body from adverse effects of API and modifying the release of API.

Chapter 17 discusses the different conducting polymer coatings used over metal surfaces for corrosion protection along with the role of conducting polymers and various coating techniques. Additionally, this chapter summarizes the performance improvement and bulk modifications of conducting polymers and extensive studies on the protective coating of conductive polymer materials are discussed.

Chapter 18 presents extensive research studies reported by worldwide scientists and specialists in the area of polymer coatings for industrial applications. New and emerging industrial applications are discussed, including microsystems, oil and gas industries, electronics, biomedical systems, pipeline, automotive industries, micro bit storage systems, anti-corrosion and antibacterial coatings.

Chapter 19 discusses recent advancements in the usage of polymers for coating of different dosage forms such as tablets, capsules, implants,

nanoparticles, and liposomes. Additionally, mechanisms of polymeric film formation and applications of polymer coatings in the different areas of biomedicine are clearly explained as are the application of different polymers in various coating functions.

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Fabrication Methods for Polymer Coatings

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Abstract

Polymer coatings mean the top layer applied on any substance for purposes like protection and decoration. It is possible to apply to synthetic materials as well as metals and ceramics. They are resistant to high temperatures, such as up to about 280°C. The polymeric coating process comprises applying a polymeric material onto a supporting substrate and coating the substrate surface. Polymeric coatings can be obtained using natural and synthetic rubber, urethane, polyvinyl chloride, acrylic, epoxy, silicone, phenolic resins or nitrocellulose, etc. There are a wide range of fabrication methods to design and construct polymer-coated materials. In this chapter, the techniques are described and discussed including blade coating, spray coating, thermal spray coating, pulsed laser deposition, plasma polymerization, flow coating, spin coating, sol–gel, dip coating, and grafting. The key point is provided to highlight current methods and recent advances in polymer coating fabrication techniques.

Keywords: Polymer coatings, fabrication methods, blade coating, spray coating, thermal spray coating, pulsed laser deposition, plasma polymerization, flow coating, spin coating, sol–gel, dip coating, and grafting

1.1 Introduction

Polymer coatings are thin polymer films that are applied to flat surfaces or irregular objectives. Protective and decorative layers can be served by these coatings [1]. They can be functional coatings such as adhesives or photographic films. They can be used as corrosion inhibitors or for decorative purposes like paints. Moreover, for modifying the surfaces, they can be utilized such as paper coatings or hydrophobic coatings.

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Polymeric coatings are known to be made of organic materials. However, they may contain metallic or ceramic grains to enhance endurance, property, or appearance [2]. They offer various properties and additional benefits, for instance, very good chemical resistance, very good blocking resistance, and excellent scratch and abrasion resistance. Besides, high gloss to matt looks, soft touch effect, noncoloring after UV exposure, excellent adhesion on metal and plastics, short drying time, fast hardness development, and easy formulation are other acquisitions of those coatings [3].

In general, polymer coatings are architected to manufacture a film of a kind of polymer. The process should be as fast as possible. The thickness is typically 1–100 μm . The type of coating method varies according to the thickness of the desired covering, the rheology of the running, and the velocity of the web [2].

1.1.1 Starting Liquid Types

Before passing through to the coating methods, it is better to explain starting liquid types to obtain an impermeable and indiscrete polymer coating deposit. Three different types of starting liquids can be used to achieve this output. These are indicated as: polymer solutions, monomer liquids, and polymer latexes [2].

1.1.1.1 *Polymer Solutions*

It is necessary to decrease the viscosity of the polymer to make it a stickable fluid. For this purpose, the polymer is decomposed in a dissolvent. The fluidity property of the solution is regulated by varying the amount of solvent in the solution. The resulting fluid is covered onto the substrate. The dissolvent should then be removed by a drying operation. The glass transition temperature of the dispersion rises with removal of the solvent. If the drying temperature is smaller than the glass transition temperature, the coating passes to the solid phase. However, when the drying temperature is higher than room temperature, it is seen that solidification or hardening continues during the cooling of the coating. On the other hand, some of the polymers can crystallize when the dissolvent is removed. While some are cooling, they form semi-crystalline final polymer coatings [2].

Generally, most polymers are insoluble in water and organic solvents are used for dissolution. The solvent is selected in terms of both its ability to

dissolve the polymer and its influence on the drying step. Due to the need to add different additives and reduce the cost, it may be necessary to use more than one volatile solvent [2].

The use of coatings produced with polymer solution is favored as they can be applied to a wide variety of polymers at the processing site specifications and formulated according to adjustable properties to produce evaluated properties in the last product. The quantity of polymeric material soluble in a solvent is relatively small. The drying requirement therefore appears as a function of the unit thickness of the coating. On the other hand, there are environmental and safety concerns due to complications related to solvent use. Solvent recycling is another important problem. It is also another disadvantage that flammable solvents need to be captured by expensive driers [2].

1.1.1.2 *Liquid Monomers*

Many monomers have fluid properties at room temperature. Therefore, there is no need to decrease their flow resistance at the coating process temperature. Also, they can be covered directly without adding any dissolvent. Oligomeric precursors can be said to be in this category. Without the need for a drying operation, the monomer liquids are allowed to solidify by serial curing reactions. Meanwhile, the molecular weight of the covering material rises in the period from progression of curing to the formation of a solid polymer layer. Hardening reactions are initiated by exposing them to energetic sources, for instance, ultraviolet light or electron beams [2].

The most widely used and popular coating material is epoxy in the field. They are not monomers, yet they are formed by a chemical reaction of oligomeric resins with its hardeners. The liquids can also be produced with dissolvent to enhance interoperability. Acrylates as liquid monomers are widely used for ultraviolet curing [2].

Monomer fluids do not require much drying step because they contain very little solvent. Therefore, they are quite attractive ways for coatings. The final coating properties (e.g., density of crosslinking) can be managed at the curing stage using parameters such as temperature, ultraviolet density, or the resin chemistry. Nevertheless, in some cases, the materials used in functional polymer solution coatings may be less expensive than monomers and initiating agents. Besides, due to the high degree of crosslinking, the final product can sometimes be brittle [2].

1.1.1.3 Polymer Latex

A latex can be defined as the dissipation of polymeric grains in water. In the case of lower water solubility of the polymeric materials having functional properties, the latex paths supply an environmentally suitable solution for forming enduring covering. Grains varying in size from ~ 10 nm to 1 μm can be manufactured from various polymeric chemicals by emulsion polymerization. It is easy to use, especially because they are synthesized in dispersion form and can be stabilized in the process. For some special applications, latex may also be formulated with other phases, such as ceramic grains [2].

The drying of the latex suspensions appears to be slightly different from the drying of the hard colloidal grains. This process is known as “film formation” depicted in Figure 1.1. Because water is removed, the grains go into the “consolidation” step and become more concentrated in suspension. When the drop time is over, surface tension, capillary, and van der Waals forces begin to pull the grains toward each other. Those forces must be powerful sufficiently to allow the grains to flatten at the grain–grain contact points. Consequently, the pores between the particles become smaller. This stage is called “compression.” The final stage is the “union” stage. Here, the polymer chains boil the particles together and transcend the boundaries between the grains. With that process, a finalized covering is formed that lacks gaps that were once between the individual particles [2].

Water is a liquid medium that can be used in latex coatings. Thus, monomer and solvent may be an eco-friendly alternative to other coatings used.

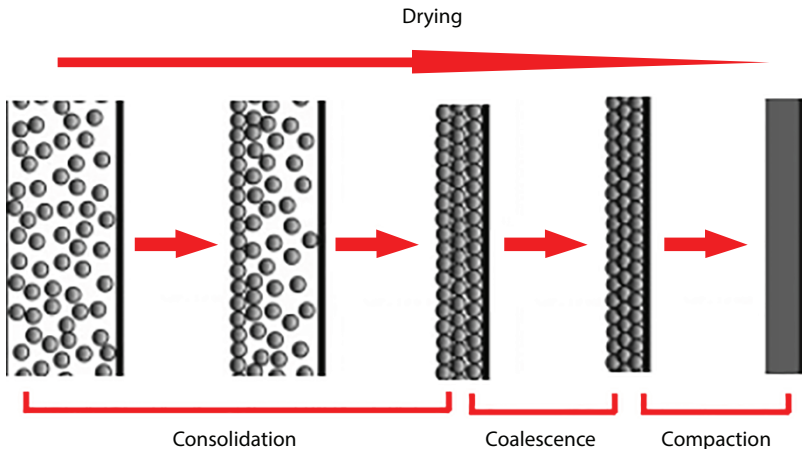


Figure 1.1 Latex film formation stages [2].

Various coatings, such as paints and varnishes, seem to start as latex dispersions. On the other hand, it is pricey to transport and purchase latexes as raw material on a commercial scale. Besides, drying of water is an operation that requires more energy [2–4].

1.1.2 Polymer Coating Methods

Coatings made of polymeric materials can provide many different surfaces: metallic, ceramic, or synthetic materials, using a number of different techniques [5]. They must adhere well to the substrate. They should also not be readily susceptible to moisture, salt, heat, or different kind of chemicals. Generally, the following properties are required for a good coating film [3]:

- Water-based resins. Low- or zero-volatile organic compounds (VOC)
- Very good stain and chemical resistance
- Very good blocking resistance
- Excellent scratch and abrasion resistance
- High gloss to matt looks
- Soft touch effect
- Nonyellowing after UV exposure
- Excellent adhesion on metal and plastics
- Carbodiimides for 2K systems

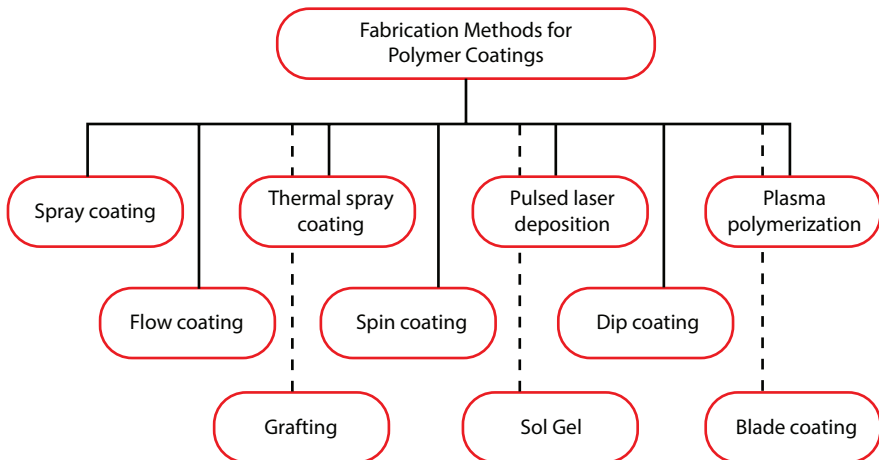


Figure 1.2 Fabrication techniques for polymer coatings.

- Short drying time, hence fast hardness development
- Easy formulation

Applied coating methods can affect the product quality, and thus the coating methods are important to obtain desired properties. Different fabrication methods are demonstrated in Figure 1.2.

1.1.2.1 Blade Coating

The blade coating can be defined as a process in which a certain amount of covering material is applied to the underside and the excess is removed by a measuring blade to obtain the desired coating thickness [6, 7]. This coating method has several advantages for obtaining a good coating film. Homogeneity of the coating area, small amount of material waste, prevention of intermediate layer melting, roll-to-roll production compliance, and economic use of the material [8–10]. In this method, fast drying process will prevent the slowing of the manufacturing process by solvent annealing [10]. Control of the thickness can be adjusted by controlling manufacturing conditions such as sol concentration, blade gap, and blade covering velocity [8].

1.1.2.2 Spray Coating

Spray coating technique is a process method in which the printing material (ink) is constrained through a nozzle and thereby forming a thin aerosol [11]. In this process, the performance of polymer solar cells seems to be limited by certain disadvantages, for instance, isolated droplets, non-uniform surfaces, and holes at some points. Regarding the process parameters, the flow rate, the pressure, the substrate temperature, the density of the mixing dissolution, the spraying time, the distance between the sample, and the air brush can be listed [6].

1.1.2.2.1 Nozzle-to-Substrate Distance

The distance between the nozzle and the surface is considered to be one of the process parameters, since it has a big effect on the morphology of the deposited part in the spray coating. Many studies were performed to examine and achieve the best distance of the nozzle and surface for the active coating. Vak *et al.* [12] found three areas between the air brush nozzle and the substrates, which were “wet,” “intermediate,” and “dry.” They then concluded that the perfect linear control distance was in the “intermediate-region.” This result is described as the spray time function.

Susanna *et al.* [13] observed that, with the same material, the deposited material remained wet when the distance between the sample and the air brush was less than 15 cm. They reported that they manufactured dry and powdered coatings over 20 cm from the substrate. In this study, the “intermediate” region was 17 cm.

1.1.2.2.2 Solvent and Mixed Solvents Effect

There are many different solvents used by scientists to investigate the effects of dissolvent on coating quality and efficiency, for example, chlorobenzene, dichlorobenzene, trichlorobenzene, p-xylene, toluene, etc. The choosing of solvent affects the choice of nozzle–substrate distance for achieving the suitable thickness and the covering morphology. It is therefore important in all spray coating methods. Fundamentally, the principle behind selecting a dissolvent should be to select a quick-drying dissolvent to inhibit droplets from redissolving the substrates. However, this velocity should not be high enough to permit a homogenous and pinhole-free coating to be formed [14].

Pin-hole thin films are not desirable in that those films impair the efficiency of the coating. The quantity of fluid sprayed on the surface must be higher than at least a threshold to produce films without pin-hole. In this way, it may be possible for the droplets placed on the surface to join into a fully wet region. [6].

1.1.2.2.3 Substrate Temperature and Annealing Treatment

Green *et al.* [15] conducted an extensive work examining the performance of spray-coated devices over the effect of annealing temperature. In this study, it was seen that the efficiency of the devices amended with annealing temperature. The change in the intensity of the short-circuit current causes this to happen. Lee *et al.* [16] showed that the morphological surfaces of spray-coated equipment were not affected by thermal annealing at a micrometer scale at 150°C. Though, conflicting results have been reported by Dang *et al.* [17]. It was found that annealing affected the morphological texture of the active regions of the rotary casting and improved toward phase separation.

1.1.2.3 Thermal Spray Coating

Thermal spraying can be defined as a method of improving the surface of a solid object. This method can be used to coat a variety of materials to

supply resistance to abrasion, erosion, cavitation, corrosion, abrasion, or heat. It can also be applied to supply electrical conductivity or insulation, lubricity, high or low friction, victim wear, chemical resistance, and many other desired features [18].

The application area of thermal spray is very wide. Extending the life of new components and repairing and reconstructing worn or damaged components may be some of them. In general, all thermal spraying methods include the adhesion of little softened grains to a dirt-free and conditioned surface to form a well coating. The combination of thermal energy and kinetic energy results in the flattening of the particles on the surface and on top of one another, with the successive layers forming an adhesive coating. Some advantages of thermal spray are shown below [18]:

- Metallurgical cold processing.
- No heat input, no deterioration.
- A mechanical bonding process required.
- Many different materials can be sprayed such as: steels, stainless steels, nickel alloys, copper, bronzes, molybdenum, ceramics, tungsten carbides, etc.
- Thickness can be applied between 100 and 750 microns, but more can be provided.
- Line of sight process.

Some of different types of thermal spray methods are used in the industry. In flame spray method, gas and oxygen are used for melting the wires before spray process with compressed air. Powder spray uses acetylene and oxygen for softening or melting the powders with the gas flow accelerating the grains to the substrate. In arc spray method, direct current (DC) electrical power is used for melting the wires before spray operation with compressed air. Plasma spray uses electric arc in an inert gas for creating a plasma that can soften the spray powders. The gas stream can project the powder onto the substrate for low oxide situation. High velocity oxygen fuel (HVOF) can use an accelerated oxygen or fuel flame for softening the spray powders and projecting them onto the surface with high levels of kinetic energy. All of the five thermal sputtering processes described above can be used to amend the substrate properties. Thanks to these engineering coatings, properties such as improved wear resistance, thermal barriers, electrical and thermal conductivity, hard chrome exchange, and insulation can be obtained on the material surfaces [18].

1.1.2.4 Pulsed Laser Deposition

The word laser is an abbreviation of light magnification with excited radiation emission. It has precious unique features such as narrow frequency bandwidth, consistency, and elevated power density. Because the light beam is too dense, it may be possible for vaporizing the hardest and heat-resistant materials. In addition, it has features such as high precision, reliability, and spatial resolution. Therefore, it has utility in the processing of thin coatings for the materials modification, heat treatment of the material surface, welding, and micro-modeling industry [19, 20].

In view of the pulsed laser deposition principle, it is generally seen that a pulsed laser beam is focused on the surface of a solid material. Electromagnetic radiation is strongly absorbed by the solid surface, which allows quick evaporation of target materials. When the content of the vaporized materials is examined, it is seen that it consists of highly excited and ionized species [21].

The pulsed laser deposition technique makes it particularly easy to store materials with complex stoichiometry. Therefore, it has attracted great interest of late years. The coating of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin film, a superconductor, was the first such process. Since then, the material, which is particularly difficult to obtain by multi-element oxides, has been successfully applied with this technique. The main advantages of this technique are [21]:

- *Conceptually quite simple:* Using a laser beam to evaporate the target surface and produce a coating of the same content as the target.
- *Versatile:* A wide range of materials can be coated in different gases over a wide gas pressure range.
- *Cost-effective:* A single laser can work with multiple vacuum systems.
- *Fast:* Good quality products can be obtained in 10 or 15 min.
- *Scalable:* Scaling can be achieved by advancing complex oxides toward volume production.

1.1.2.5 Plasma Polymerization

Plasma polymerization can be described that, in this process, organic and inorganic polymers can be deposited from a monomer vapor using

an electron beam, ultraviolet radiation, or radiation discharge [22]. For low pressure plasma coating, it is ensured that gas or liquid monomers are processed, which are polymerized under the action of plasma. In general, the coating thicknesses obtained are in the range of one micrometer. The adhesion of the coatings to the surface is quite good [23].

When it is examined to activate and degrease, the process is much more complex. For example, barrier coatings are produced in fuel tanks, scratch-resistant coatings in headlights, and hydrophobic coatings. There are three coating methods used in large-scale applications [23]: hydrophobic coatings, PTFE (polytetrafluoroethylene)-like coatings, and hydrophilic coatings.

Coating of metals by plasma polymerization allows various effects such as continuous activation and functional coatings for one to several weeks. Process parameters should be set to take into account the characteristics of some equipment, such as generator type and power, electrode assembly, and material properties of the workpiece.

Plastics can be simply coated by plasma polymerization. In this way, a scratch-resistant coating can be made to CDs and DVDs without damaging their quality. If the products have low friction, PTFE-like coatings can be used to increase this. It may also be possible to bind functional groups such as amino groups used for bioanalytical applications to the plastic surface.

The difficulty in coating materials such as glass and ceramics is to prepare the surface accordingly. Once this problem is solved, there is no other element to prevent the application of the coatings. Check the adhesion of the covering to the surface in all cases. Where “mismatch” occurs between the coating and the substrate material, it may be ensured that the intermediate layers are applied as a binder. It is known that textile materials are very well-coated in plasma. However, the difficulty here lies in the long-term protection of coatings against surfactants. If hydrophobic coating is desired, fluorine-containing gases or monomers may be used [22, 23].

1.1.2.6 *Flow Coating*

The flow coating technique is a suitable form of coating to form polymer coating thickness gradients in the submicron regime. The device has a fixed blade that is fixed in a gap above a moving stage. The height of this gap can vary from tens of microns to hundreds of microns. The surface to be covered is firmly fixed to the stage, and the grains of a polymer

dissolution are deposited between the blade and the surface and compacted. Next, the blade is accelerated relative to the surface. In the flow coating technique, the polymer is drawn through the substrate under forces caused by capillary forces holding between the fixed blade and the substrate, and by friction on the same solution as the blade. This process is in principle similar to the other measured flows for instance dip coating and blade coating.

In the fluid coating process, the capillary forces ensure that the polymer dissolution is kept under the knife at the first state at zero speed. In progress of time, the volume gradually decreases because of the evaporation of the dissolvent from the edges. At lower speeds, frictional pull may cause material to escape under the blade, although the capillary forces are intended to hold the material between the surface and the blade. This material then dries by evaporation of the solvent and is left in the shape of a wet coating [24–26].

1.1.2.7 *Spin Coating*

The spin coating method is a very common technique for applying thin coatings to the surfaces. It is seen that this technique is used in many different industries and technology branches. The most significant benefit of spin coating is the ability to manufacture very smooth coatings quickly and easily. The thickness of these films can range from several nanometres to several microns. The use of spin coatings is particularly common in organic electronics and nanotechnology. This production is based on many methods that can be utilized in different semiconductor industries [27, 28].

1.1.2.7.1 General Theory

In the spin coating process, it can be expressed as applying the desired material by pouring it onto the surface of a substrate and coating it evenly along its surface as it rotates in a solvent (an “ink”) (Figure 1.3). As the coating liquid is dropped to the center of the target, the stage begins to rotate. As the rotation accelerates, the resulting centrifugal force allows the liquid to spread over the entire surface to form the coating layer. Factors such as the viscosity of the fluid, the rotational speed of the target, the acceleration of rotation, and the aeration that affect the drying rate affect the thickness of the film formed [29].

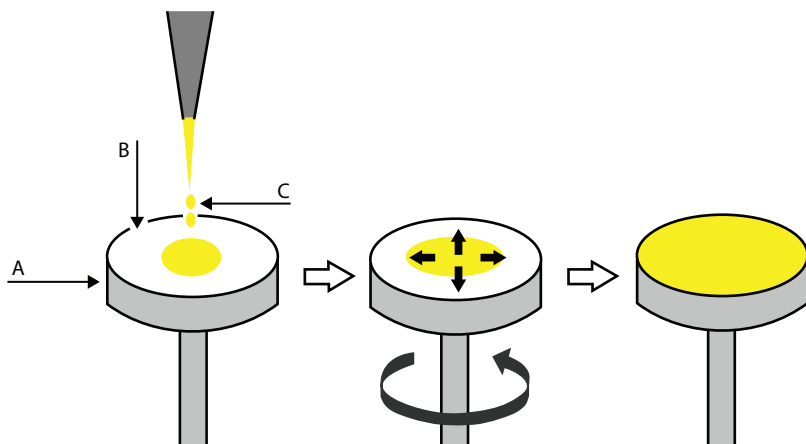


Figure 1.3 A coating specimen obtained by spin coating a small molecule in solution by using a static dispersion (A. Rotating stage. B. Target surface. C. Coating fluid.) [29].

1.1.2.7.2 Applications

Spin coatings can vary greatly when viewed as a field of application. They can be used to cover surfaces smaller than a few square millimeters used in the state of the art, as well as to flat panel TVs with a diameter of 1 m or more. When evaluated as a coating material, it is possible to coat substrates such as photoresists, insulators, organic semiconductors, synthetic metals, nanomaterials, metal and metal oxide precursors, transparent conductive oxides, and many other different materials.

1.1.2.7.3 Advantages and Limitations

Combined with a thin and homogeneous coating, the greatest advantage in the spin coating process can be shown as the simplicity and relative ease of installation of a process. The high air flow caused by the high rotational speeds causes rapid drying. This helps ensure high stability in macroscopic or nano-length scales.

A single substrate is used for spin coating. This is the limitation of this process. Therefore, the yield seems lower than roll-to-roll operations. Certain nanotechnologies require time for self-assembly and/or crystallization. Fast drying times in spin coating can therefore lead to poor performance.

1.1.2.7.4 Spin Speed

The current rotational speed ranges are important because they define the thickness range that can be obtained from a particular solution. By rotating the coating, it is possible to produce homogeneous films relatively easily from about 1000 rpm. However, high quality coatings can be obtained with caution up to 500 or 600 rpm and sometimes lower than this.

1.1.2.7.5 Coating Duration

In general, standard spin coatings allow the substrate to spin until the film is completely dry. However, the boiling point and vapor pressure of the dissolvent utilized, as well as the environmental parameters in which the extrusion coating is made, such as temperature and humidity, affect this. A spin coating time of 30 s is recommended as a starting point for most processes, since this is considered to be sufficient [28].

1.1.2.8 Sol-Gel

Sol-gel technology can be defined as the use of liquid solutions to produce solid films with a wide chemical composition structure on various substrates at relatively low temperatures. Sol-gel-coated coatings are very diverse in function, for example, electrical conductivity, superconductivity, ferroelectric behavior, corrosion resistance, selective barrier for wear resistance and gas permeability, etc. There are many interdependent or independent factors that determine the manufacturing and specialties of sol-gel coatings [30].

Historically, the first synthesis of silica gel goes back to 1846. However, it is seen that sol-gel chemistry has been comprehensively researched ever since the 1970s. In the sol-gel method, chemical reactions of the basic precursor, which is usually an organometallic compound, are used in alcoholic dissolutions. These reactions produce various inorganic networks that can be constituted from a metal alkoxide dissolution [31, 32].

The sol-gel method has three steps for the production of the latest metal oxide protocols: these are hydrolysis, condensation, and drying. The operation begins by subjecting the metallic precursor to rapid hydrolysis to manufacture the metal hydroxide solution. In the following step, condensation occurs, leading to the constitution of a three-dimensional gel. After drying the obtained gel, the product obtained can be quite easily transformed to

Xerogel or Aerogel depending on the drying mode. The structure of metal precursors and solvents in the sol–gel process has an effective role in metal oxide synthesis. The sol–gel method can be classified in two ways, depending on the nature of the solvent used: aqueous sol–gel and anhydrous sol–gel method. If water is used as the reaction media, the aqueous solution is the method. However, if organic solvent is utilized as the reaction media, it is called anhydrous sol–gel. Figure 1.4 shows the reaction steps used for the manufacturing of metal oxide nanostructures in the sol–gel technique [33, 34].

The production steps of a radar-absorbing covering material manufactured by the sol–gel coating technique are shown in Figure 1.5. In this study, barium hexaferrite particles were synthesized by sol–gel [35, 36]. The precursors used were barium nitrate ($\text{Ba}(\text{NO}_3)_2$) and ferric citrate monohydrate ($\text{C}_6\text{H}_5\text{FeO}_7 \cdot \text{H}_2\text{O}$), chelating agent citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), and pH regulator ammonium hydroxide (NH_4OH). Firstly, the process began by dissolving the ferric citrate and barium nitrate separately in citric acid. Using a magnetic stirrer, the solutions were vigorously stirred until a clear dissolution was achieved. Ammonium hydroxide was inserted to the dissolution until the pH reached 7 to ensure homogeneous suspension and stable pH. Next, the dissolution was held in a water bath at 80°C for 15 h in air to remove the water slowly from the solution. In this way, a high-viscosity wet gel was obtained. The wet gel obtained to prepare the dry gel was kept in an oven at 180°C for 15 h. Finally, in the

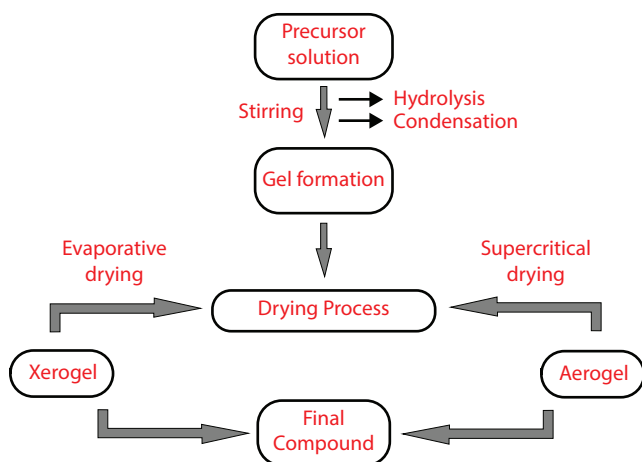


Figure 1.4 Reaction pathway for production of metal oxides in the sol–gel [33].

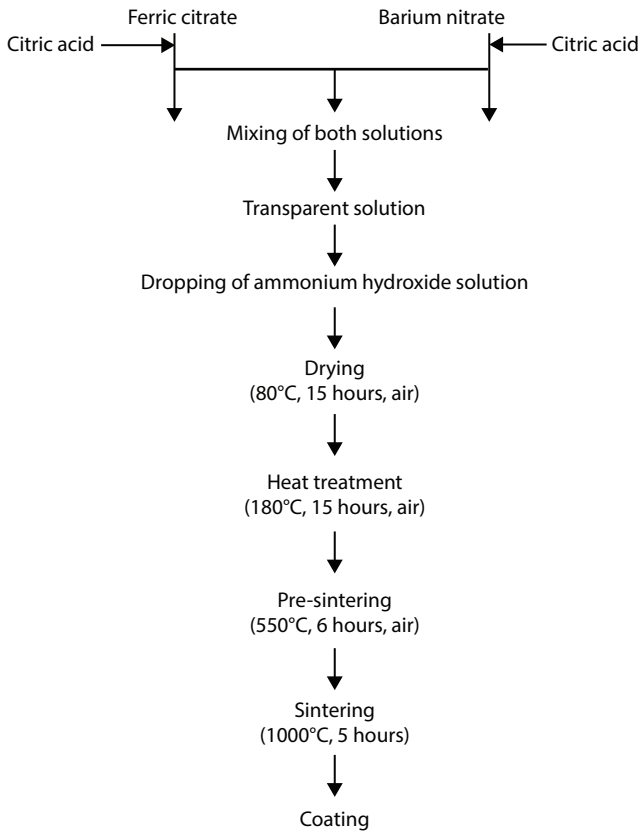


Figure 1.5 Coating is produced by sol-gel method [37].

sintering step, sintering was first performed at 550°C for 6 h to evaporate the impurities of the dry gel. The process was then completed by sintering in a tube oven at 1000°C for 5 h [37, 38].

1.1.2.9 Dip Coating

Immersion coating is considered one of the earliest mercantile available processes. The primitive patent in that field was given to Jenaer Glaswerk Schott in 1939 for sol-gel reproduced silica films [39, 40]. Today, it is seen that this technique is used for various applications such as sol-gel derived coatings, ferroelectrics, dielectrics, sensors and actuators, membranes, superconducting layers, protective coatings, and passivation layers. The process is described by three important technical steps:

1. *Immersion and dwell time:* At this stage, it is ensured that the substrate is kept in the coating solution for sufficient wetting for sufficient interaction. For this purpose, the surface is immersed in the precursor dissolution at a stable rate and then allowed to stand for a certain period of time.
2. *Deposition and drainage:* At this stage, film deposition is made. By pulling the substrate upward with a stable velocity, a thin precursor solution layer is retained. Excess fluid is discharged from the surface.
3. *Evaporation:* The dissolvent vaporizes from the liquid in this step. The deposited thin film may be supported by heated drying.

This is the fluid that forms it. Heat treatment is then carried out to burn the residual organics. In addition, the heat treatment carried out in this step may provide to crystallize the functional oxides.

Although that covering technique appears to be quite simple, microscopic processes need to be understood in more detail during immersion coating to adapt the final coatings. There is an important connection between the construction of the dissolution or the formed sol and the microstructure of the deposited coating. This is the coating process that establishes the connection. In the standard operation, the substrate is drawn upright from the solution tank with a stable velocity [41]. With the movement of the moving substrate, the liquid is dragged through a mechanical boundary layer based on the current line [42].

The flux moving upward is compensated by evaporation. As a result, the position of the film and the film remain constant relative to the surface of the coating bath. Upon evaporation and discharge of the solvent, the film has an approximately wedge-like shape terminating in a drying line. The vapor–solid–solid three-phase limit herein is defined as the drying line. Above this line, the nonvolatile species form the deposited part, which may be exposed to further curing. After gradual concentration of the inorganic species by evaporation, agglomeration and gelation occur to formalize a kind of dry gel or xerogel layer. The process ends with the final drying [39].

1.1.2.10 Grafting

This method is a capable tool for achieving surface grafting, surface modification, and functionality of polymer brushes on a solid surface. The final functionalized polymer chains can be grafted onto the solid surface, which is referred to as grafting. This grafting reaction may proceed with surface

polymerization. In this way, a thin polymer brush layer is formed on the solid surface, which adjudicates the surface features. By combining surface roughness with mixed brushes, interchangeable ultrahydrophobic surfaces can be obtained [43].

The composition of surfaces and interfaces has a very important status in determining the performance of the materials. For example, areas of critical importance include the control of surface and interface properties, colloid stabilization, adhesion, lubrication, rheology, immobilization of catalysts, and the production of multiphase materials [44]. In addition to these classic areas, surface modification has lately played an important role in bioengineering, nonlinear optics, (bio) sensors, nano patterning, molecular recognition, waveguides, and electronic microcircuit operations. Accumulation of surface-bound thin polymer layers with convenient physical and chemical features for optimizing surface properties is one of the first operations [45].

The process is due to the elevated surface density, the precise placement of the chain on the surface, and the easy and controllable insertion of polymer chains with prolonged durability of the grafted layers. The most important benefit is the fact that several different polymers are attached to the same substrate. Prevention of macro-phase separation is achieved by chemical grafting. The features of the coating are determined by the consolidation of particular functional components. Polymer brushes are formed when the linked polymer chains contacted to the solid substrate with a chain end reach a relatively high grafting density. This can be clearly noticeable from other grafted polymer layers. Because of the excluded volume effect, the brush-like layers are formed when the surface is completely coated with a comparatively dense grafted chain monolayer normally stretched to the support. Parameters such as graft density, chain length, and chemical content of the chains can control the brush features [43, 46].

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Fabrication Methods of Organic/ Inorganic Nanocomposite Coatings

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Abstract

In recent years, nanocomposite coatings have displays increasing interest due to its applications like electronic, defense, aeronautical and automotive industries. The nanocomposite coatings offer efficient and cost effectiveness coatings with excellent properties such as corrosion, wear, heat resistive properties, and higher mechanical strength. Compare to the conventional methods of composite coatings, it provides higher performance with ease of fabrication methods. In this chapter different fabrication techniques have discussed with appropriate schematic diagrams. The different organic/inorganic matrices and nanofillers have listing in table. The various nanocomposite coatings has discussed namely, sol-gel method, cold spray technique, chemical vapor deposition, physical vapor deposition, thermal spray coatings, electroplating deposition and electroless deposition methods.

Keywords: Nanocomposite, sol-gel method, cold spray technique, chemical vapor deposition, physical vapor deposition, thermal spray coatings, electroplating deposition, electroless deposition

Abbreviations

O/I	-	organic/inorganic
PEG	-	Polyethylene Glycol

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PBZ	-	Rubber-modified polybenzoxazine
TMOS	-	Polymers containing reactive trimethoxysilyl
PVDF	-	Polyvinylidene fluoride
ETFE	-	Ethylene tetrafluoroethylene
PANi	-	Polyaniline
PPy	-	Polypyrrole
PVA	-	Polyvinyl Alcohol
CNT	-	Carbon Nanotubes
PEO	-	Poly ethylene oxide
PTFE	-	Polytetrafluoroethylene

2.1 Introduction

The blending of organic and inorganic constitutions is a most general approach to obtain surface coatings with optimal properties. The two elements with different or same essential properties are mixed at micro, nano, or molecular level. The composite coatings have appeared like general coatings with an opaque appearance. OINC stands for organic-inorganic nanocomposite coatings, which is nano scale hybrid coatings depend on organic matrix. In the earlier 15 years, research on organic-inorganic nano composite coatings has been increasing randomly in both academic and industrial fields. Many researchers published more papers related to nano composites coatings. The nanocomposite comprises two phases of materials, namely, matrix and fillers. Fillers are disseminated in matrix material [1]. Classification of nanocomposite is based on different types of filler materials and matrix materials. The nano structured fillers are classified into three types, namely, zero-dimensional, one-dimensional, and two-dimensional nano fillers. Zero-dimensional nano structured fillers are in the form of nano particles, and one-dimensional and two-dimensional nano structures are in the form of nano tubes and nano layers, respectively.

The matrix materials are categorized into two main groups, namely, organic and inorganic. The four major classifications of nanocomposite coatings are as follows: organic/inorganic (O/I) nano composite coating, organic/organic (O/O) nano composite coating, inorganic/organic nano (I/O) composite coating, and inorganic/inorganic (I/I) nano composite coatings.

The other name of organic based nano composite coatings called polymer based nano composite coatings. The different polymer materials are listed in Table 2.1. Various nano fillers utilized for nano composite coatings are listed in Table 2.2. Different organic nanocomposite materials are listed in Table 2.3.

Table 2.1 Different polymer-based matrix materials.

Matrix	References
Epoxy	[2–7]
Polyethylene Glycol (PEG)	[8–11]
Polyurethane	[12, 13]
Polyamic Acid and polyimide	[14]
Chitosan	[15, 16]
Rubber-modified polybenzoxazine (PBZ)	[17]
Polymers containing reactive trimethoxysilyl (TMOS)	[18]
Polyvinylidene fluoride (PVDF)	[19]
Pullulan	[20]
Fluoroacrylic polymer	[21, 22]
Ethylene tetrafluoroethylene (ETFE)	[23]
Polyaniline (PANi)	[24–26]
Polyacrylate	[3]
Polycarbonate	[27]
Polypyrrole (PPy)	[27–30]
Polyester	[31]
Polystyrene	[32]
Poly(n-vinyl carbazole)	[33]
Fluorinated Polysiloxane	[34]
Polyacrylic	[35]
UV-curable polymers	[36]
Polyamide	[37]
Polydimethylsiloxane	[38]
Polyvinyl Alcohol (PVA)	[39]

Table 2.2 Different inorganic nano fillers used in nanocomposite coatings.

Inorganic nano fillers	References
Clay	[4, 31]
Carbides	[40]
Borides	[41]
Metallic particles	[24, 42]
Nitrites	[43–50]
Oxides	[4, 51, 52]
Nano-diamond	[53, 54]
Carbon Nanotubes (CNT)	[55]

Table 2.3 Different organic nano fillers used in nanocomposite coatings.

Organic nano fillers	References
Poly ethylene oxide (PEO)	[56]
Polyaniline (PANi)	[23]
Polytetrafluoroethylene (PTFE)	[57–59]
Nano-cellulose and Cellulose Nano-crystal	[25, 36]

2.1.1 Transparency of Organic/Inorganic Nanocomposites

Equation (2.1) can be used to calculate transmissions of light through non-homogeneous coatings like organic-inorganic nano composite coatings. This equation is based on Rayleigh scattering theory, where, L denotes thickness of the coatings, r_p is the radius of the scattering element, ϕ_p volume fraction, λ denotes wavelength of the light, n_p indicates refractive indices of the inorganic phase and n_m denotes refractive indices of the polymer matrix. Transparency of the organic inorganic nano composite is high since size of the inorganic phase is lesser compared to wavelength of light.

$$T = \exp \left[- \frac{3\phi_p L r_p^3}{4\lambda^4} \left(\frac{n_p}{n_m} - 1 \right) \right] \quad (2.1)$$

2.2 Fabrication Methods

Different fabrication methods of nanocomposite coatings are briefly discussed below; it includes sol-gel method, cold spray technique, chemical vapor deposition, physical vapor deposition, thermal spray coatings, electroplating deposition, and electroless deposition methods.

2.2.1 Sol-Gel Method

Sol-gel method is one of physical deposition methods. The nano composite coating is very much appropriate to attain good quality of coatings upto micro-scale level. This methods exhibit few draw backs that include crack formation and thickness restrictions. Further, heat treatment is also critical. If coating thickness is greater than the critical thickness value, tensile stresses may induce in coating material, and it leads to crack formation. The sol-gel chemistry has employed to generate I/O nanocomposite coatings. The nano composite coatings have formed in the form of inorganic nano fillers dispersed in an organic matrix. An extensive variety of oligomers and low molecular weight of organic compounds are used as organic matrix materials. Silanes and organic molecules have combined and form nanocomposite coatings which comprise nanoparticles. Inorganic and organic nano composites have been interlinking by coupling agents.

In sol-gel technology, different coatings methods exist, namely, flow coating, spray coating, spin coating, and dip coating technologies. The different stages of dip coatings are shown in Figure 2.1. The dip coating technique has performed under controlled atmosphere. First step of dip coating technique is dipping the substrate into the initial solution. At controlled speed, withdrawn of substrate has performed. The inner structure and film thickness of coating has influenced by withdrawal speed and evaporation conditions. The solution is uniformly spreading on the surface of the substrate by joined effect of capillarity and viscous drag. The effect of characteristic of the films has applied more on post heat treatment of the coated substrates.

2.2.2 Cold Spray Technique

Figure 2.2 shows the principle of cold spray technique for preparation of nano composite. Copper and CNT, nano composite coatings, have fabricated on the copper plate of thickness 0.3 mm. The cold spray technique system consist of different parts, namely, pressure gas supply, heater, powder feeder, de laval-type nozzle, xy axis movable table, and

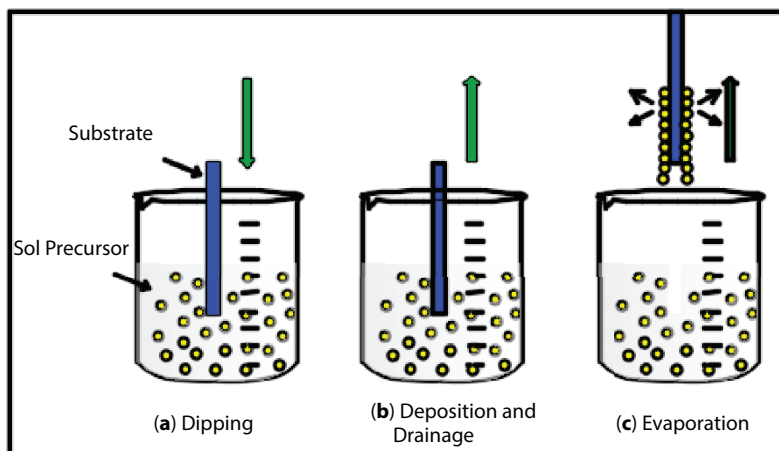


Figure 2.1 Sequential stages of the dip-coating technique for thin film deposition: (a) the substrate has dipped and immersed in the sol precursor, (b) the substrate has withdrawn at constant speed rate, and (c) solvent evaporation yields to the gelation of the layer [60].

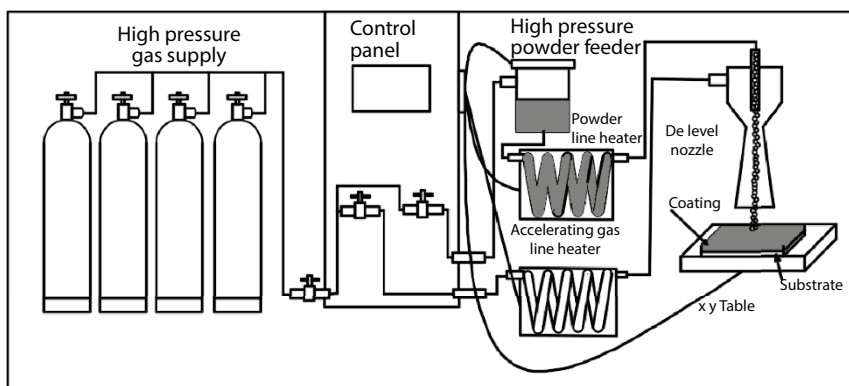


Figure 2.2 Principle of cold spray technique for preparation of nanocomposite [62].

control panel. The feed disc speed 7.5 rpm and mass expended in feeder disc determine feed rate of powder. This method of fabrication of coating materials has performed with low melting temperature of sprayed materials. The cold spray method of fabrication of coating material is not a conventional thermal spray coating methods like plasma, gas flame, and detonation spraying. Since the process has performed at low temperature, it avoids oxidation, decomposition, and phase changing during

the process. The attained coatings having low oxygen concentration and low porosity compared to conventional spray coating methods. In other words, this coating method has high strength and higher interfacial bonding strength. This method is also applicable for the metallic matrix materials like copper [41, 55], aluminum [53, 61], cobalt [40], or alloy matrix [43–45], and nanofillers, namely, carbide, carbon nano tubes, and diamond [40, 41, 43–45, 53, 55, 61].

2.2.3 Chemical Vapor Deposition

The chemical vapor deposition process initiates with materials in tanks (red, blue, and cyan colors). These materials are utilizing to building blocks of the required nanocomposite coatings on the surface of substrate. The materials are coated by melting or reducing the pressure and then transferred to vacuum chamber, which containing materials to be coated on substrate. Speed up the process of converting the monomers to polymers by linking up in chains on the surface of materials. Figure 2.3 shows principle of chemical vapor deposition method. This method can be used for inorganic to inorganic nano composite coatings [63–65] and organic to inorganic nano composite coatings (platinum (II) hexafluoroacetate as precursors) [66]. Aerosol assisted chemical vapor deposition

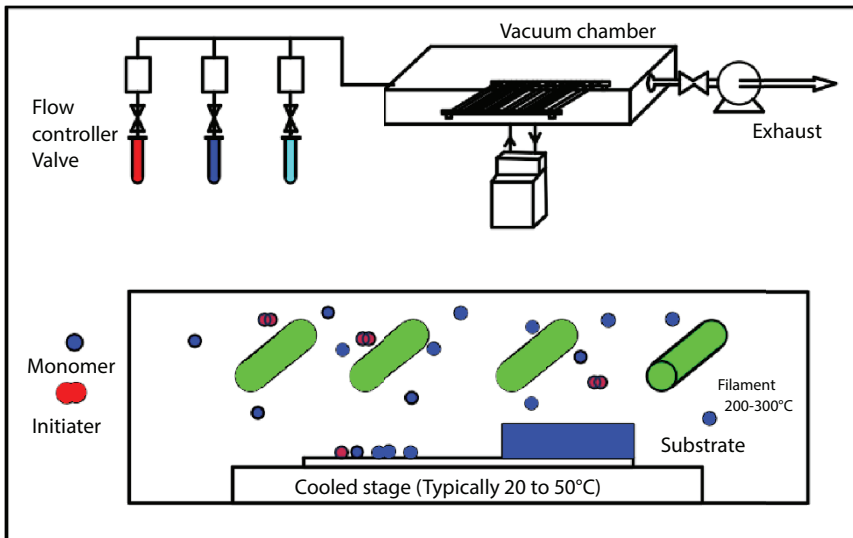


Figure 2.3 Principle of chemical vapor deposition method.

method [67] can be used to increase quality of coatings. A specific advantage of this method is used to fabricate high quality films.

2.2.4 Physical Vapor Deposition

The physical vapors deposition method includes thermal evaporation [68], ion implantation [69, 70], laser ablation [71], and laser assisted deposition [72]. This technique is suitable for inorganic and inorganic nanocomposite coatings [73–78] and organic and inorganic nanocomposite coatings. Schild [72] has introduced the nanocomposite coatings by aerosol assisted plasma deposition. Figure 2.4 shows basic principle of physical vapor deposition method. The physical vapor deposition process has utilized to fabricate nanocomposite coatings in the range from nanometers to micrometers. This method comprising three basic steps has listed below:

- ✓ Evaporation of the materials from a solid phase has been performing by gaseous plasma.
- ✓ Vacuum or partial vacuum has transferred to the surface of the substrate.
- ✓ Fabricate thin film on the surface of substrate by condensation.

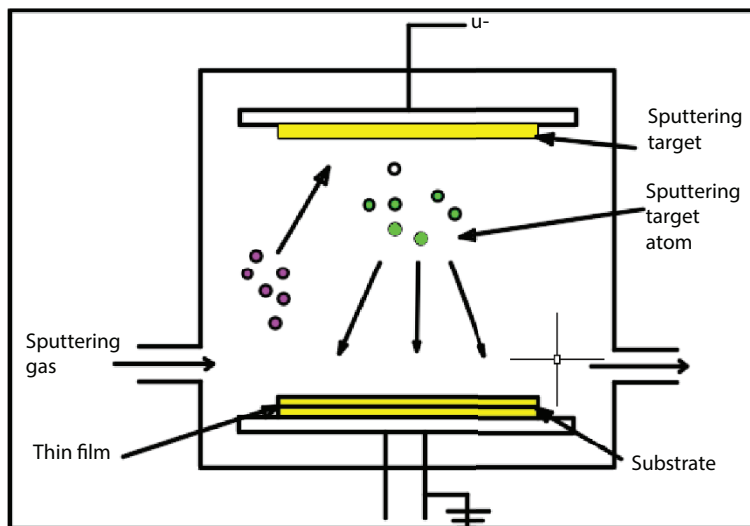


Figure 2.4 Principle of physical vapor deposition method.

The most generally utilized coating methods in physical vapor deposition methods are sputtering and evaporation methods. Sputtering is one of plasma assisted coating technique in which vapor is generated by bombardment of gaseous ions. The evaporation method is another method of generating vapor by heating materials using suitable method in vapor. The condensation mechanism has used to deposits coating material on the surface of the substrate.

2.2.5 Thermal Spray Coating

Different materials used in thermal spray coating process, namely, polymers, metallic, ceramic, and cermet. The materials have transferred to a torch or gun in the form of powders or wire or rod with above or equal to molten temperature of materials. The molten state materials are projected in a gas stream on the substrate surface. The quality of the coatings has determined by different parameters, namely, surface roughness, toughness, surface hardness, adhesive strength, coating density, and oxide contents. The most significant advantage of thermal spray coatings are wide range of coating materials and substrate materials. The coatings can be removed without any damage on the substrate and recoating can performed on the substrate surface. One of disadvantage of this method is that small or tiny and complicated shapes are difficult to coat on the substrate surface. Figure 2.5 shows general diagram of the thermal spray coating method.

2.2.6 Electrodeposition Method

The electrodeposition method can be used to fabricate nano composite coatings which include organic nanofillers, namely, PEO and PTFE [56, 57, 79] and inorganic matrices [80–84] or organic matrices [85]. Figure 2.6 shows principle of electrodeposition method.

Many papers has summarized the electrochemical method of nano composite coatings [1, 86–101].

The different organic matrices, namely, polyelectrolytes and polyethyleneimine, are electrochemically deposited on the inorganic substrate such as metal ions and ceramic nanomaterials. Compared to traditional methods of coatings, nano composite coatings displays higher hardness and heat resistive property due to presence of nano particles on the outer boundaries, it also restricts movements of ions and also recrystallization at higher temperatures.

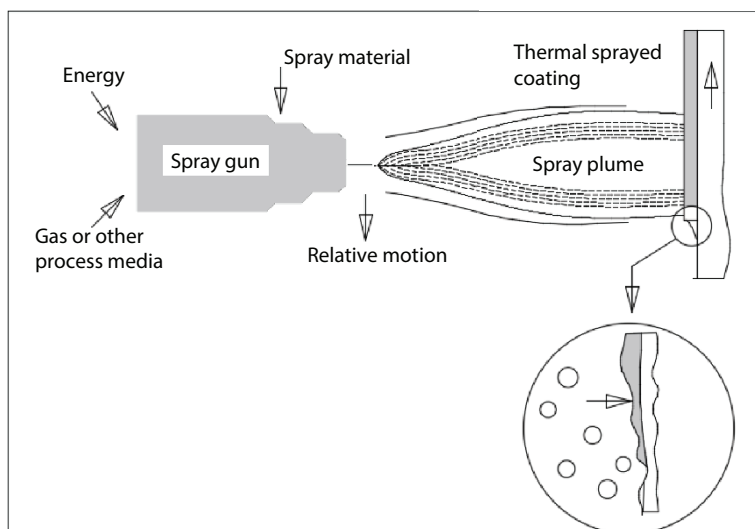


Figure 2.5 General schematic diagram of thermal spray coating processes.

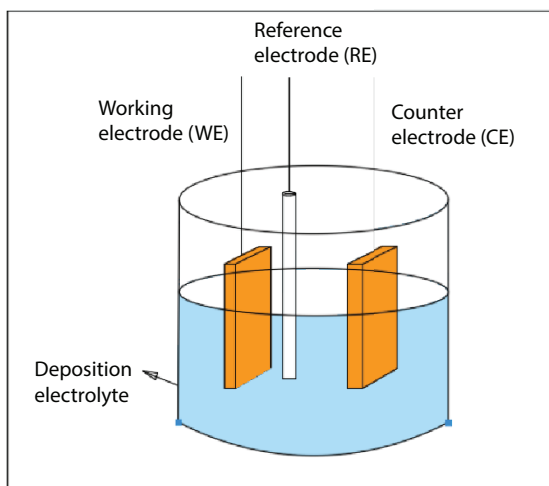


Figure 2.6 Principle of electrodeposition method.

2.2.7 Electroless Coating Method

Electroless deposition is a chemical reduction technique, in which metals like aluminium, iron and silver are coated on the fiber surface as metal ions in an aqueous solution without use of electrical energy. In this process,

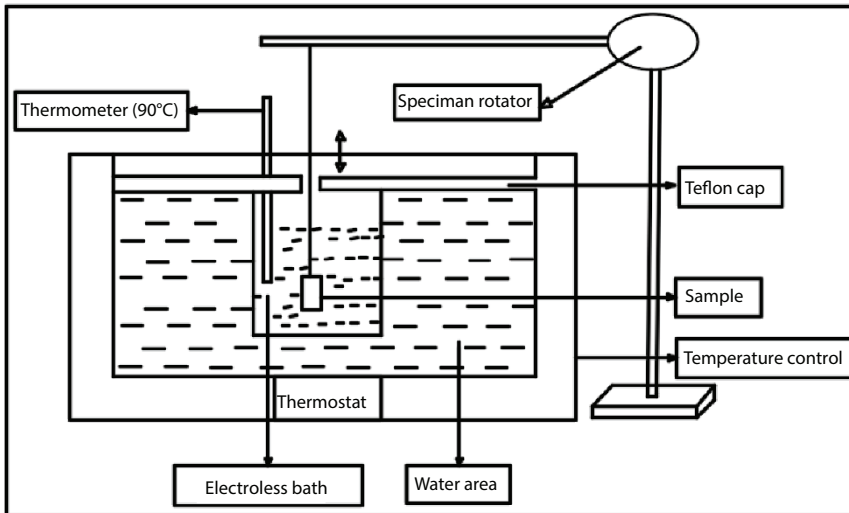


Figure 2.7 Principle of electroless coatings experimental setup.

metal ions act as electron acceptor and metal act as electron donors. Figure 2.7 shows the principle of electroless coating experimental setup. Fibers treatments by physical or chemical methods are necessary for good interaction between the electroplated layers on the surfaces. Electroless deposition process is one of most accepted methods of fabricating nano composite coatings due to its excellent corrosion [102–104], wear resistance [105, 106], and also different applications like soldering and welding applications.

2.3 Conclusions

Nowadays, nanocomposite coatings become cost effective without compromising performance. The nanocomposite coating fields are expected to cover larger application in future. The composite coatings provide enhancing properties of the materials like antibacterial, scratch resistive coatings, reflective coatings, and fire retardation properties. Classification of different coatings methods has been summarized with different coating techniques. The transparency of organic and inorganic nanocomposites has discussed. In future, smart coatings can be used as multifunctional coatings including photovoltaic cell, solar-based thermal applications, and solar-to-fuel conversion.

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Dry Powder Coating Techniques and Role of Force Controlling Agents in Aerosol

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Abstract

Presently, diverse methods have been well studied for the design and fabrication of versatile powder and particles. However, these techniques have few limitations on account of the need for complex manufacturing setup, the extensive volume of starting materials, and the use of toxic reagents which have a decisive impact on our ecosystem. Therefore, to surpass such issues, material scientists have explored single-step, eco-friendly dry powder coating techniques. Dry powder coating assists to develop powders and particles with miscellaneous functionalities. The present chapter underlines the importance of dry powder coating technique in the field of aerosols particularly dry powder inhaler. This chapter also contains a section detailing the process analytical techniques, the force controlling agents, advancement in medical device coating, and the use of numerical simulation in coating technology. This chapter is the first comprehensive account of dry powder coating techniques in the discipline of dry powder inhalers. Therefore, it can be of likely significance for both the industry as well as academia.

Keywords: Dry powder inhalers, aerosol, dry powder coating, mechanofusion, force controlling agents, cohesive-adhesive balance, deagglomeration, magnesium stearate

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Abbreviations

World health organization (WHO); tuberculosis (TB); lower respiratory tract infection (LRTI); chronic obstructive pulmonary disease (COPD); novel drug delivery systems (NDDS); dry powder inhalers (DPI); pressurized meter dose inhalers (pMDIs); soft mist inhalers (SMIs); cohesive-adhesive balance (CAB); spray drying (SD); dry powder coating (DPC); process analytical techniques (PAT); force controlling agents (FCAs); magnesium stearate (MgSt); Leucine (LEU); magnetically assisted impaction coating (MAIC); turbo rapid variable (TRV); X-ray photoelectron spectroscopy (XPS); rotating fluidized bed coater (RFBC); atomic force microscopy (AFM); inverse gas chromatography (IGC); quality by design (QbD); real time release (RTR); critical quality attributes (CQA); critical process parameters (CPP); glass transition temperature (T_g); hydroxypropyl methylcellulose (HPMC); polytetrafluoroethylene (PTFE); discrete element method (DEM).

3.1 Introduction

Pulmonary ailments are one of the prevailing worldwide community health crises [1]. They are described by airflow limitation, chronic inflammation, bronchoconstriction, loss of elasticity, mucus hypersecretion, and emphysema [2, 3]. Numerous factors such as air pollution (fine and ultrafine particulate matter), tobacco smoke, biomass fuels, inhalation of toxic particles, dust particles, occupational chemicals, systemic diseases, and genetics issues are responsible for the progression of pulmonary diseases [3, 4]. Recent statistics presented by the World Health Organization (WHO) showed that >235 million people suffered from respiratory diseases with >3 million mortalities reported annually due to the same [5]. A few of the most ordinary and occupational pulmonary diseases are chronic obstructive pulmonary disease (COPD), tuberculosis (TB), cystic fibrosis, pulmonary emphysema, asthma, lung cancer, pulmonary hypertension, and lower respiratory tract infection (LRTI) [6]. By knowing the severity of the diseases, various active researchers and clinicians thoroughly investigated the different drug molecules (e.g., synthetic molecules, derivatives, isolated phytoconstituents, and herbal extracts) [7–10] along with the dosage forms (e.g., tablet, capsules, and suspension) for treatment of pulmonary diseases [11]. Additionally, several novel drug delivery systems (NDDS) such as polymeric nanoparticles, lipid nanoparticles, microspheres, polymer-drug conjugates, micellar systems, and lipid vesicles were

also systemically studied and clinically investigated for the management of pulmonary diseases [12]. However, by considering the pathophysiology of lung diseases and biology of the pulmonary airways, inhalation is a conceptually more suitable delivery route to augment therapeutic efficacy and patient compliance in the treatment of pulmonary diseases.

Various conventional dosage forms such as dry powder inhalers (DPI), soft mist inhalers (SMIs), pressurized meter dose inhalers (pMDIs), and nebulizers are well studied and explored for various pulmonary ailments and pathophysiological conditions [11]. DPIs have several key advantages of physicochemical stability, no need for cold chain storage, drug deposition using the patient's respiration, and the superior prospect of particle engineering as compared to other dosage forms. DPIs are the drug/device combination product comprised of three main elements, i.e., micronized drug (0.5–5 μm), right carrier (90–120 μm), and aerosol device (unit or multi-dose). From a formulation perspective, carrier molecules are more important owing to the small mass of drug (e.g., 18 mcg; Spiriva® HandiHaler®, Boehringer Ingelheim) within the final formulation [11, 13]. Cohesive-adhesive balance (CAB) between drug and carrier is fundamental for satisfactory deagglomeration of DPIs. Moreover, there are several physicochemical attributes such as carrier size, morphology, true density, and interface properties that are decisive for the satisfactory dispersion/deagglomeration of DPIs. The carrier physicochemical attributes influence the DPIs performance at different levels: molecular, particulate, and delivery. Thus, formulation scientists have taken several efforts to modify the carrier physicochemical properties in order to control the DPIs therapeutic outcome. These efforts mainly involve modification of carrier molecule using several novel processing techniques such as antisolvent crystallization [14], antisolvent crystallization using binary solvents [15], liquid crystalline phase [16], supercritical fluid crystallization [17], ultrasound-assisted crystallization [18], electrospinning assisted crystallization [19], and spray drying (SD) [20, 21]. However, these techniques have few limitations on account of the need for complex manufacturing setup, dedicated machinery, need for a large amount of starting materials which is time-consuming [22–24]. Additionally, scale-up issues and regulatory requirements make these processes more complicated [24]. To avoid such processing issues, scale-up challenges, and technical complications, material scientists explored the dry powder coating (DPC) techniques.

DPC is one-step, eco-friendly, and easy to scale-up technique wherein the physicochemical properties of carrier molecules are modified. It is a solvent-free powder processing method. DPC help to develop powders and particles with miscellaneous functionalities and properties. In DPC,

equally dispersed, fine guest particles above the surface of larger host particles can be fabricated with desired properties. Acceptable blending uniformity and CAB can be achieved by modifying the carrier physicochemical properties through the DPC technique. Apart from this, various other key benefits (adequate homogeneity, flowability improvement, and dispersibility enhancement) can be achieved using DPC [25, 26].

The present chapter deals with DPC methodology and high/low shear techniques used in powder processing. This chapter also contains a dedicated section dealing with various process analytical techniques (PAT) for ensuring DPC process uniformity and consistency. Additionally, the various force controlling agents (FCAs) used in DPC is also thoroughly discussed with particular emphasis on DPIs aerodynamic performance. Furthermore, this chapter also underlines the importance of the inhaler device and capsule coating to enhance aerodynamic functioning on DPIs. In the concluding section of the chapter, significance along with applications of numerical simulation in DPC is also summarized. This chapter is the first inclusive account of dry powder coating (DPC), coating techniques, and force controlling agents (FCA) used in DPIs.

3.2 Dry Powder Coating

Dry powder coating (DPC) presents numerous key benefits such as providing a homogenous free-flowing blend, enhanced content uniformity, and low risk of contamination. Functionalized particles fabricated by DPC have tailored physicochemical properties such as improved flowability, enhanced dispersibility, good wettability, and better solubility. Moreover, it also shows improvement in catalytic, electrical, and optical properties of the final blend. Furthermore, enrichment of color, flavor, and appearance has also been well documented [25]. DPC technique is an energy-saving and eco-friendly process since it does not need any specific treatment or pre-conditioning with organic solvents or an extra drying process. In some DPC techniques, where milling is sync with coating, there is less possibility of external contamination in absence of milling aid (metal balls, glass beads) [25, 27–29].

DPC is a simple, high-shear progression wherein fine guest particles are coated to the exterior of larger host particles. Fabrication of functionalized particles using DPC technique is generally performed in three steps: de-agglomeration of the cohesive guest particles (step 1), the formation of interactive mixtures (step 2) and the redistribution of guest particles within-host particles to attain homogeneous distribution of guest particles

(step 3) [30–32]. Physical or chemical types of interfacial forces are mainly present between host and guest particles during processing. DPC concept can be described as composite powder formation, micro-fabrication, mechanical treatment, hybrid mixing, mechanical dry coating, surface adsorption, engineered particles, and encapsulation phenomenon. DPC can be divided into different classes as per the extent of coating action (i) discrete (partial coating), (ii) steady film construction, as well as (iii) uninterrupted coating (encapsulation). Figure 3.1 illustrates the different types of dry powder coated particles. During DPC, absolute facade treatment can be achieved when the kinetic energy provided through DPC machine/technique is adequate to deagglomerate guest particles by offering centripetal force as well as energy for particle-particle interaction ensuring uniform and steady adsorption of fine guest molecules across the surface of host particles. However, the nature and degree of DPC is also equally dependent on the physical attributes of the guest particles

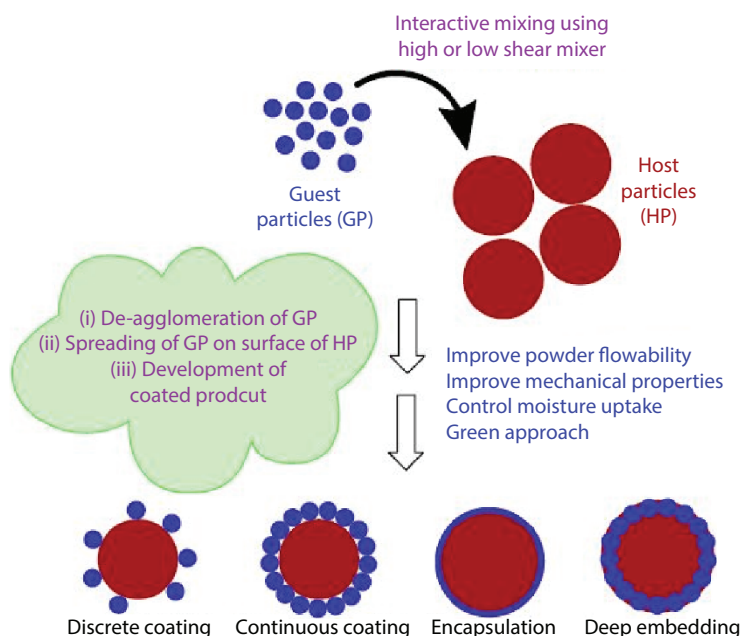


Figure 3.1 Graphical representation of dry powder coating modified after Dahmash *et al.*, 2015 [25] [Diagram represents the process of dry powder coating and types of coated particle. It is a simple and eco-friendly approach for designing multifunctional particles. Uniform coating can be achieved using high as well as low shear mixing techniques. The inner part (red-colored) is the coarse host particle while the outer part (blue colored) is the fine guest particle.]

(size, morphology, surface properties, roughness, and melting point) and mechanism involved in DPC [25, 28, 29]. In the subsequent section, various DPC processing equipments and techniques are described with particular importance on mechanism and shear rate.

3.3 Dry Powder Coating Techniques

Albeit the manufacturing steps, the formulation of an active pharmaceutical ingredient (API) or guest substance with other excipients needs to be mixed homogeneously for better pharmaceutical applications. Various tools and techniques (high shear or low shear) are available for ordered mixing or the development of interactive mixtures. High shear mixing relies on a high-intensity mixing blade while low shear mixing uses the planetary movement of the mixer arm to generate homogeneity [25]. Mechanical tumbling, cube mixer, turbula mixer, and V-blender are the commonly used techniques at laboratory scale for achieving ordered mixing. Additionally, various advanced techniques such as cyclomix, magnetically assisted impaction coating (MAIC), and/or turbo rapid variable (TRV) mixer are also explored for the development of interactive mixtures [25, 26]. These techniques can be classified on the basis of shear forces and/or mechanisms involved in DPC. Various commonly used DPC strategies are enlisted in Table 3.1.

Several high shear techniques (e.g., mechanofusion, hybridizer, TRV) are well reported in the scientific literature for DPC. Mechanofusion equipment is one of the well-known and widely applied methods for achieving uniform and reliable DPC. Mechanofusion equipment consists of a rotating cylindrical vessel and a scraper. Mechanofusion devices typically produce high mechanical shear action using a combination of sufficiently high compression and centrifugal forces causing surface interaction (or fusion) of guests and host particles. As the cylindrical assembly spin at a greater momentum, the forceful communication produces a large amount of kinetic energy with the development of a consistent guest particle layer over the host particles [30, 34]. Hybridizer is a next-generation coating technique pertinent to producing high shear mixing and milling for effective deagglomeration of guest particles followed by its uniform layering on to the host particles. It is made up of high-speed motor, a mixing vessel equipped with six blades, a powder recirculation circuit, and a coolant jacket to control the heat generated during the process. Uniform coating is achieved due to high shear action, diffusion forces, and heat produced during friction between the powder, the blades, and the vessel walls.

Table 3.1 Summary of DPC technologies with their important advantages and limitations [25, 26, 33].

Technology and manufacturer	Shear and speed	Advantages	Limitations
Mechanofusion and Hosokawa, Japan	High shear and 200 to 10,000 RPM	1. Allow fusion (physical and/or chemical) between guest and host.	1. Not suitable for thermo-labile substances and fragile host material. 2. Heat generation may lead to polymorphic transformation.
Hybridiser and Nara Machinery, Japan	High shear and 5,000 to 20,000 RPM	1. Very short processing time. 2. Powder recirculating unit guarantee homogeneity of the final blend. 3. Can work with smaller host (0.1 μm) particles.	1. Not suitable for thermo-labile substances and fragile host material. 2. Not suitable for a continuous process. 3. Heat generation may lead to polymorphic transformation.
Cyclomix	High shear and 30 m/s (Rotor speed)	1. Produces mild coating. 2. Used for coating, mixing and granulation	1. There is particle attrition or even rupture of host materials. 2. Not appropriate for unstable or brittle host materials

(Continued)

Table 3.1 Summary of DPC technologies with their important advantages and limitations [25, 26, 33]. (*Continued*)

Technology and manufacturer	Shear and speed	Advantages	Limitations
Turbo rapid variable (TRV) and GEA Group, Germany	High shear and 20 m/s (impeller tip speed)	1. Work on a single, bottom driven impeller. 2. Suitable for continuous process and scale-up. 3. Ensure homogeneity of the final blend.	1. Not suitable for thermo-labile substances and fragile host materials.
PMA™ and GEA Group, Germany	High shear	1. PMA is a bottom-drive high shear mixer. 2. Useful for blending, melt or wet pelletizing and granulation	–
Magnetically assisted impaction coating (MAIC) and Aveka, USA	High shear	1. Allow the least variation in particle shape or size. 2. Utilize a magnetic field and thus lower energy needs. 3. The minor amount of heat is generated thus suitable for thermo-labile substances	1. A significant risk of contamination due to magnetic particles. 2. Not suitable for a continuous process.

(*Continued*)

Table 3.1 Summary of DPC technologies with their important advantages and limitations [25, 26, 33]. (*Continued*)

Technology and manufacturer	Shear and speed	Advantages	Limitations
Theta composer and Tokuju, Japan	Low shear (soft coating) and 30 RPM (vessel speed); 500–3,000 RPM (rotor speed)	1. Short processing time (2 to 10 min). 2. Allow minor change in particle shape or size. 3. Low heat generation and thus no thermal deterioration. 4. Suitable for batch type process.	1. Not appropriate for a continuous coating process.
Rotating Fluidized Bed Coater (RFBC) and NJIT, USA	Low shear (soft coating)	1. Suitable for both batches as well as continuous type coating process. 2. Can be utilized for very small guest and host substances.	1. Surplus aerosolization of the fine guest particles.
Turbula shaker mixer and Glen Mills Inc., USA	Low shear	1. Mixing is achieved in a closed container and thus provide dust-free blending and lower contamination risk. 2. Good powder homogeneity of the mixture owing to interaction, translation, rotation and inversion as per the geometric theory in relation to Schatz.	–

(*Continued*)

Table 3.1 Summary of DPC technologies with their important advantages and limitations [25, 26, 33]. (*Continued*)

Technology and manufacturer	Shear and speed	Advantages	Limitations
Fluid energy mill (FEM) and Sturtevant Inc., USA	Micronization with the coating	1. Can be used for nano and micron-sized guest and host substances. 2. Suitable for continuous type process.	1. Pre-mixing is required prior to FEM. 2. May lead to polymorphic transformation. 3. Need to monitor various parameters such as feeding rate, feeding and grinding pressure to ensure the formation of uniform mixture or coating.

Both these techniques support physical and chemical guest-host interactions termed as mechanochemistry [28, 29]. TRV is a high speed mixing unit composed of a single, bottom driven impeller drive. It is largely apt for the rapid mixing or coating of small quantities of API with base excipients, distinctive of inhalable products. By integrating the directional effects of the feeder blade with the high surface area of the main impeller blade, rapid uniform mixture is obtained in a reproducible way. It is available in various capacities (1, 5, 10, 20, 30, and 60 L) for batch as well as continuous manufacturing processes [35]. Various patents on TRV-based inhalation products are listed in Table 3.2.

Similar to high shear techniques, several low shear techniques were also available for DPC to achieve coating at mild conditions. Low shear techniques are mainly preferred for thermo-labile substances and fragile host material owing to controlled heat generation, compaction energy, and shear forces during coating or mixing [25]. Elliptical rotor mixer (Theta Composer) and rotating fluidized bed coater (RFBC) are the commonly used low shear techniques for DPC. In theta composer, powder coating is achieved due to compression between the elliptical vessel wall and rotor

Table 3.2 Various Turbo rapid variable (TRV) process based dry powder formulations.

Guest substances	Host substances	Key findings	Reference
Magnesium stearate	Lactose monohydrate and triphenylacetate	Achieved good blend uniformity for low dose (1 to 400 mcg) DPI formulation	[36]
Fluticasone furoate	Lactose monohydrate	Achieved uniform mixing for low dose DPI formulation	[37]
Magnesium stearate	Lactose monohydrate	Ensured uniform mixing of magnesium stearate and lactose to control chemical degradation of a drug	[38]

moving in the opposite direction [39], whereas in RFBC, uniform powder coating is produced as a result of centrifugal fluidization with the radial flow of inert gas [40]. Furthermore, the inert fluidizing gases help to enhance the collision among particles that ease de-agglomeration along with the consistent coating.

3.4 Analytical Techniques for Ensuring Coating Uniformity

The transition of particles across the powder bed during the DPC has a crucial role in the dynamics of the coating. Apt characterization of the coating quality is decisive for the superior process adaptation and optimization [41]. Comprehension of the particle dynamics can lead to a better knowledge of the overall DPC mechanism. To assess the particle dynamics, specifically high-resolution analytical tools and methods are often essential. This is mainly factual for coating analysis wherein surface energetics, surface rigidity, and surface morphology are assessed along with the

calculation of the inter-particulate forces. Over the period of time, process analytical technology (PAT) like X-ray photoelectron spectroscopy (XPS), Raman analysis (in-line or on-line), atomic force microscopy (AFM), scanning electron microscopy (SEM), inverse gas chromatography (IGC) assist in understanding particle dynamics [42, 43].

US FDA defined PAT system for designing, analyzing, and monitoring manufacturing via in process measurements of critical quality and performance attributes of materials and methods with the assurance of final product quality [44]. It is a helpful and effective move toward process validation. It merges few advanced systems, tools, and procedures, for example, quality by design (QbD), root cause analysis (RCA), Pareto chart, real-time release (RTR), and total quality management (TQM) that can facilitate offline and online authentication of vital process factors. From implementation viewpoint, PAT involves three basic steps, i.e., (i) design, (ii) analysis, and (iii) control [45, 46]. PAT allows a better understanding of the critical quality attributes (CQA) and critical process parameters (CPP). In brief, PAT provides a well-structured policy for the process screening and therefore can be implemented for better process understanding as well as risk management [46]. By knowing these facts, Table 3.3 reviews the sophisticated analytical tools and techniques that have been explored in the understanding and characterization of the DPC process and particle dynamics.

3.5 Force Controlling Agents

Force controlling agents (FCAs) are commonly used in various pharmaceutical processes. They are chemically inert, odorless, and tasteless. Different types of FCAs are explored for pre-formulation and formulation development activities, i.e., (a) metallic salts of fatty acids, (b) inorganic materials, (c) polymers, (d) alkyl sulfates, (e) fatty acids, fatty alcohols, and hydrocarbons, and (f) fatty acid esters [49]. Apart from these, several natural, semi-synthetic and synthetic pulmonary surfactants or hydrophilic surface-active molecules are also utilized as FCAs (Table 3.4). When these substances are used in pulmonary formulations, they easily dispersed over the large surface of the pulmonary airways. It is assumed that this immediate diffusion and dispersion of surfactants might facilitate drug diffusion across the lung and accordingly improve clinical outcomes. Table 3.5 enlists various investigations on inhalation powders containing FCAs. Commonly used FCAs in inhalation products are thoroughly described in the subsequent section.

Table 3.3 List of sophisticated analytical techniques for understanding dry powder coating process and particle dynamics.

Technique	Advantages	Limitations	References
Atomic force Microscopy (AFM)	1. Determine surface properties at the submicron level. 2. Available in various mode, i.e., Tapping (intermittent) or contact mode (topographical analysis); Nano-indentation mode (for elastic modulus and deformation studies); Force distance measurements (for adhesion analysis) and Colloidal probe AFM (for adhesion analysis and particle surface energetics). 3. In DPs mainly used to determine cohesive adhesive balance (CAB) between drug/guest and carrier	1. Needs specialized staff for analysis and interpretation 2. Applicable only for small particle size (nanoscale guest and submicron host) and 3. Expensive	[42, 47]
Brunauer-Emmett-Teller (BET)	1. Recognize reduction in specific surface area (SSA) and pore size before and after coating 2. Quantify the optimum level of guest material essential to achieve a uniform coating	1. Not appropriate for thermolabile substances material 2. Needs pre-conditioning for analysis	[43]

(Continued)

Table 3.3 List of sophisticated analytical techniques for understanding dry powder coating process and particle dynamics.
(Continued)

Technique	Advantages	Limitations	References
Fourier-transform infrared spectroscopy (FTIR)	1. Spot the physicochemical interaction between guest and host particles	1. Needs specialized staff for analysis and interpretation	[43]
Inverse gas chromatography (IGC)	1. Determine surface energetics at a dispersive and specific level. 2. Suitable for thermolabile material 3. It can be is combined with other surface characterization methods to study surface properties	1. Needs specialized staff for analysis and interpretation 2. Expensive in nature	[48]
Scanning electron microscopy (SEM)	1. Qualitative analysis of the degree of coating 2. A very small amount of sample needed 3. Allow visual analysis of the extent of coating and qualitative in nature	1. Needs pre-conditioning for analysis	[43]

(Continued)

Table 3.3 List of sophisticated analytical techniques for understanding dry powder coating process and particle dynamics.
(Continued)

Technique	Advantages	Limitations	References
Positron emission particle tracking (PEPT)	1. It allows a quantitative analysis of the motion of particles. 2. It can be used to conclude the location of the individual particle accurately.	1. Needs specialized staff for analysis and interpretation 2. Expensive	[43]
Radioactive particle tracking (RPT)	1. It can be used to quantitative analysis of dynamics of particles within dry-coating device 2. It can be combined with different detectors to capture the response	1. Expensive	[43]
Electron Dispersion X-Ray Spectroscopy (EDX or EDS)	1. It gives the concentration of elements present in a sample. 2. In combination with SEM, can provide better visual analysis of coated guest material	1. Not appropriate for thermolabile substance 2. Small contamination might vary the outcome	[43]

(Continued)

Table 3.3 List of sophisticated analytical techniques for understanding dry powder coating process and particle dynamics.
(Continued)

Technique	Advantages	Limitations	References
X-ray photoelectron spectroscopy (XPS)	1. It gives near-surface region elemental composition (2–10 nm depth) 2. High accuracy and specificity 3. More sensitive as compared to EDX	1. Needs specialized staff for analysis and interpretation 2. Not appropriate for thermolabile substances 3. Small contamination might vary the outcome 4. Expensive	[43]
Time-of-flight secondary ion mass spectrometry (TOF-SIMS)	1. It gives near-surface region elemental composition (2–5 nm depth) 2. Ultrahigh sensitivity and specificity 3. Need a very small sample for analysis	1. Needs specialized staff for analysis and interpretation 2. Small contamination might vary the outcome 3. Expensive	[43]

Table 3.4 Force controlling agents (FCA) [26].

Class	FCA
Amino acids	L-Leucine, D-Leucine, iso leucine, trileucine, methionine, lysine, valine, phenylalanine, aspartame or acesulfame K, and acesulfame potassium
Natural and synthetic lung surfactants lipids and phospholipids	Phosphatidylglycerol (PG), dipalmitoyl phosphatidylcholine (DPPC), dipalmitoyl phosphatidylethanolamine (DPPE), acyl substituted phospholipids, diacyl substituted phospholipids, dipalmitoyl phosphatidylinositol (DPPI), lecithin, lecithin-derivatives, soya lecithin, laxiric acid, magnesium lauryl sulfate (MLS), and sodium lauryl sulfate (SLS), triglycerides, i.e., hydrogenated castor oil waxy powder (Cutina® HR) and microcrystalline triglyceride (Dynasan® 118)
Saturated fatty acid	Erucic acid, stearic acid, palmitic acid, oleic acid, glyceryl behenate, lauric acid, and behenic acid
Natural and synthetic minerals	Talc, silicon dioxide, aluminum dioxide, titanium dioxide, and starch
Metal stearates and derivatives	Sodium stearyl fumarate (SSF), zinc stearate, magnesium stearate, lithium stearate, calcium stearate, sodium stearate, and sodium stearyl lactylate (SSL)

3.5.1 Metal Stearates

Magnesium stearate (MgSt), aluminum stearate, sodium stearate, zinc stearate, and calcium stearate are commonly used metal stearates in pharmaceutical industries [60]. Among them, MgSt is the most commonly used FCA in DPIs. Various characteristic features of MgSt are displayed in Figure 3.2. MgSt is well-known and widely used functional ingredient in pharmaceutical products, cosmetics preparations, and a variety of foodstuffs. It is obtained from vegetable as well as animal resources and available as trihydrate, dihydrate, anhydrate, and amorphous forms. It is mainly used as a lubricant in conventional oral dosage forms such as powder, tablet, granules, and capsules [61]. In DPI formulations, MgSt act as a lubricant, force controlling agent, surface control agents, water barrier or stabilizer [62].

Chemical name: Octadecanoic acid magnesium salt

Appearance: Very fine, light white, implapable powder with low bulk density, greasy to the touch and easily adheres to the skin

Chemical Formula: $C_{36}H_{70}MgO_4$

Molecular weight: 591.2436 g/mol

Density: 0.159 g/cm³ (bulk)

Melting point: 126-130°C

Specific surface area : 1.6-14.8 m²/g

Solubility: Practically insoluble in water

Flowability: Poorly flowing, cohesive powder

Safety : Nontoxic following oral administration

Lethal dose: LD₅₀ (rat, inhalation) : >2 mg/L and LD₅₀ (rat,oral): >10 g/kg

IGG Limits : 0.13 mg (Approved for inhalation products)

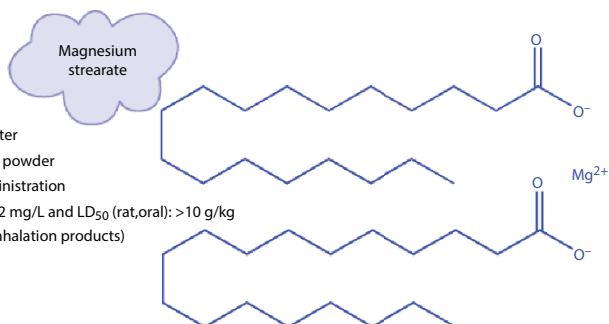


Figure 3.2 Key features of magnesium stearate for dry powder coating [Figure shows the key physical, chemical, and biological properties of magnesium stearate for successful pulmonary drug delivery].

As shown in Table 3.5, MgSt is widely used in DPI products as a tertiary ingredient. It shows promising aerosolization results by modifying the interface interaction between the micronized drug (<5 μm) particles and coarse carrier (70–150 μm) particles. Principally, MgSt regulates the inter-particulate interactions and/or CAB [62]. Another key mechanism of improved aerosolization is the dissipation of electrostatic charge on powder mixture or the formation of easily dispersible drug-excipient agglomerates [53]. It is well documented that the hydrophobization of materials with MgSt reduces the force of adhesion appreciably. More specifically, MgSt reduces the adhesion forces owing to interfacial long-range Van der Waals forces acting among the powder particles. During DPC, MgSt shapes a nanometer layering against the carrier particles which regulate the adhesive interactions between the micronized drug and sieved carrier thereby, supporting the detachment of API from the carrier upon aerosolization [53]. However, these effects are highly concentration-dependent. An optimum MgSt content is a concentration that enhances powder flow the most and results in uniform film formation to enclose the individual particle. Beyond the optimum MgSt concentration, there is a sharp drop in flowability with increased film thickness or when excess fine particles are present [26, 53]. Additionally, the specific surface area and particle size distribution (mainly, d_{50}) of MgSt are the key factors influencing its coating efficiency [60]. Moreover, MgSt is also studied to improve stability by controlling the ingress of moisture [26, 53]. By knowing these anti-adherents, anti-friction properties, and ability to modify the drug/carrier interfacial properties, MgSt is used in various commercial DPIs products (Table 3.6).

Table 3.5 Summary of inhalation powders containing FCAs.

Drug	Coating techniques	Key ingredients/ FCA	Device and flow rate (l/min)	Percentage FPF	Reference
SBS	Mechanofusion® (Rotor-type mixer)	5% MgSt	MI device and 60	69.00	[50]
SX	Mechanofusion® (Rotor-type mixer)	5% MgSt	MI device and 60	73.10	[50]
SBS	Mechanofusion®	5% MgSt	Monohaler® and 60	2.8 micron (MMAD)	[51]
Budesonide	Mechanofusion®	5% MgSt	Monohaler® and 60	2.2 micron (MMAD)	[51]
Tobramycin	Spray drying	1% Sodium Stearate	Aerolizer® and 60	84.30	[52]
SBS	Turbula® T2F mixer	10% MgSt	Rotahaler® and 60	12.6	[53]
Triamcinolone acetoneide	AMS-Mini mechanofusion with Nobilta module	5% MgSt	MI device and 60	51.60	[54]
Triamcinolone acetoneide	AMS-Mini mechanofusion with Nanocular module	5% MgSt	MI device and 60	48.30	[54]
SX	AMS-Mini mechanofusion with Nobilta module	5% MgSt	MI device and 60	73.10	[54]

(Continued)

Table 3.5 Summary of inhalation powders containing FCAs. (*Continued*)

Drug	Coating techniques	Key ingredients/ FCA	Device and flow rate (l/min)	Percentage FPF	Reference
SX	AMS-Mini mechanofusion with Nanocular module	5% MgSt	MI device and 60	69.30	[54]
SBS	AMS-Mini mechanofusion with Nobilta module	5% MgSt	MI and 60	68.60	[54]
SBS	AMS-Mini mechanofusion with Nanocular module	5% MgSt	MI device and 60	68.50	[54]
SBS	AMS-Mini mechanofusion with Nobilta module	2% MgSt	MI device and 60	75.4	[54]
FP	Collette MicroGral (High-shear)	Respitose® ML001 and 5% MgSt	Breezhaler® and 90	32.2	[55]
FP	Turbula® T2F mixer (Low-shear)	Respitose® ML001 and 10% MgSt	Breezhaler® and 90	26.10	[55]
SX	Collette MicroGral (High-shear)	Respitose® ML001 and 0.1% MgSt	Breezhaler® and 90	56.70	[55]
SX	Turbula® T2F mixer (Low-shear)	Respitose® ML001 and 0.5% MgSt	Breezhaler® and 90	56.30	[55]
SBS	Theta-Composer®	Pharmatose® 200M and 10% MgSt	Jethaler® and 30	~40.00	[56]

(Continued)

Table 3.5 Summary of inhalation powders containing FCAs. (*Continued*)

Drug	Coating techniques	Key ingredients/ FCA	Device and flow rate (l/min)	Percentage FPF	Reference
SBS	Theta-Composer [®]	Pharmatose [®] 200M and sucrose tri-stearate (J-1803F, 10%)	Jethaler [®] and 60	46.86	[53]
SBS	Wurster Fluidized Bed	Pharmatose [®] 200M (13%) aqueous solution containing HPMC (2%)	Jethaler [®] and 60	34.9	[57]
SBS	Vortex-Mixer	Pharmatose [®] 200M and 2% MgSt	Jethaler [®] and 60	26.0	[58]
TNRA	*Rotor-type powder mixer	Pharmatose [®] 325M and 1% Sucrose stearate	Jethaler [®] and 30	20.90	[59]
TNRA	*Rotor-type powder mixer	Pharmatose [®] 325M and 2% MgSt	Jethaler [®] and 30	34.60	[59]

SBS: salbutamol sulfate; MgSt: magnesium stearate; MI: Monodose inhaler; FPF: fine particle fraction; FP: fluticasone propionate; SX: salmeterol xinafoate; TNRA: triple neurokinin receptor antagonist and MMAD: mass median aerodynamic diameter.

Table 3.6 Commercial DPIs products containing magnesium stearate.

Market	Proprietary name	Active ingredient and dose	Company
European Union	Seebri® Breezhaler®	Glycopyrronium bromide (44 mcg)	Novartis Pharmaceuticals, UK Ltd.
European Union	Ultibro® Breezhaler®	Glycopyrronium bromide (85 mcg) and indacaterol maleate (43 mcg)	Novartis Pharmaceuticals, UK Ltd.
European Union	*Fostair NEXThaler®	Beclometasone dipropionate (100 mcg) and formoterol fumarate dihydrate (6 mcg)	Chiesi Ltd.
European Union	Incruse Ellipta®	Umeclidinium bromide (55 mcg)	Glaxo Smith Kline, UK
European Union	Anoro Ellipta®	Vilanterol trifenate (55 mcg) and umeclidinium bromide (22 mcg)	Glaxo Smith Kline, UK
European Union	Relvar Ellipta®	Fluticasone furoate (184 mcg) and vilanterol trifenate (22 mcg)	Glaxo Smith Kline, UK
European Union	Trelegy Ellipta®	Fluticasone furoate (92 mcg), vilanterol trifenate (55 mcg) and umeclidinium bromide (22 mcg)	Glaxo Smith Kline, UK
United States	Utibron®	Glycopyrrolate (15.6 mcg) and indacaterol maleate (27.5 mcg)	Sunovion Pharmaceuticals Inc.

*Available in 200/6 mcg strength.

3.5.2 Amino Acids

Amino acids (AA) are the endogenous, natural compounds which may have fewer safety problems for drug targeting or delivery to the pulmonary airways. AA and/or derivatives have a suitable molecular weight (0.25 to 1,000 kDa) and therapeutic properties for pulmonary therapy. Moreover, AA's isomers and racemic mixtures may be used for formulation development and drug delivery [26, 56]. A superior amount of AA can modify the aerosolization pattern of potent antibiotics exclusive of apparent cytotoxicity [26]. Moreover, AA and derivatives are used as stabilizers for various bio-molecular formulations employing potent biomolecules and bacteriophages [56]. In the case of DPIs, leucine (LEU) is the most frequently explored ingredient.

The aerodynamic outcome of particles and powders can be enhanced by applying a surface layer of hydrophobic amino acid, i.e., LEU [63, 64]. During co-SD with a drug, LEU is known to supersaturate quickly and provide a surface coating to drug particles [65]. LEU shows good lubrication properties for inhalable powders and particles. LEU (5%) often leads to the fabrication of irregular (wrinkled/corrugated) particles [66]. Such particle structure with reduced inter-particulate interaction provides better CAB as compared to smooth particle [66]. Together, corrugated particles showed a mean particle size suitable for pulmonary delivery. Hence, particles surface covered by LEU generally has superior flow properties, dispersion, as well as aerosolizing behavior [56]. Table 3.7 enlists various investigations on inhalation powders containing LEU. As shown in Table 3.7, LEU was also utilized in mixture among additional ingredients. Within a binary or ternary powder system with a suitable sugar carrier (lactose/mannitol/trehalose), LEU helps to stabilize biomacromolecules and enhance the aerosolization performance [67]. It also acts as a drug dispersion enhancer for chitosan containing customized drug release preparation including various molecules such as curcumin [68], diltiazem hydrochloride [69], and levofloxacin [70]. Recently, spray-dried capreomycin: LEU (80:20) inhalation powder was explored in a clinical study to manage TB [81]. In brief, on the basis of the final concentration, method of preparation and chemical nature of the drug, LEU can act as an aerosol enhancer, stabilizer, and flow enhancer.

Trileucine is a tri-peptide produced from three L-LEU residues. It is another essential amino acid used in DPI formulations. As compared to leucine, it has a high glass transition temperature (T_g) (104°C), which demonstrate better physicochemical sturdiness of trileucine. T_g of SD trileucine is highly dependent on the pH and concentration of anions,

Table 3.7 Summary of inhalation powders containing amino acids as FCAs.

Formulation system	Method/technique	Key ingredients/ amino acids	Device and flow rate (l/min)	Percentage FPF	Reference
Mannitol	SD	Leucine	Monodose inhaler and 60	80.10	[71]
Mannitol	SD	Leucine (10%)	Monodose inhaler and 60	80.46	[71]
Trehalose	SD	Leucine (10%)	Monodose inhaler and 60	66.51	[71]
Curcumin-nanoparticle	SFD	Leucine, chitosan and mannitol	Powder entrainment tube and 85	49.10	[72]
Diltiazem hydrochloride nanoparticle	W/O emulsification	Chitosan, leucine	Rotahaler® and 60	21.00	[73]
Levofloxacin microparticles	SD	Chitosan, leucine (4:1)	Cyclohaler® and 60	52.24	[74]
Isoniazid nanoparticles	SD	Chitosan, leucine (10%), tripolyphosphate	Cyclohaler® and 60	45.00	[75]
Immune globulin G	SD	Cysteine (50%)	Cyclohaler® and 60	70.51	[76]

(Continued)

Table 3.7 Summary of inhalation powders containing amino acids as FCAs. (*Continued*)

Formulation system	Method/technique	Key ingredients/ amino acids	Device and flow rate (l/min)	Percentage FPF	Reference
Immune globulin G	SD	Phenylalanine (50%)	Cyclohaler® and 60	62.43	[76]
Immune globulin G	SD	Leucine (50%)	Cyclohaler® and 60	58.68	[76]
Gentamicin	SD	Trileucine (2%)	PDS and 28.3	46.80	[77]
Gentamicin	SD	Trileucine (15%)	PDS and 28.3	49.30	[77]
Netilmicin	SD	Trileucine (2%)	PDS and 28.3	48.80	[77]
Netilmicin	SD	Trileucine (15%)	PDS and 28.3	62.40	[77]
Budesonide	SD	D-leucine (1%)	RS01 model 7 and 60	30.07	[78]
Disodium cromoglycate	SD	Leucine (2%)	Osmohaler® and 100	71.90	[79]
Disodium cromoglycate	SD	Methionine (40%)	Osmohaler® and 100	62.42	[80]

FPF: fine particle fraction; SD: Spray drying; SFD: Spray freeze-drying and PDS: pulmonary delivery system (Nektar Therapeutics, CA).

cations, and zwitterions of the system. The dispersibility of trileucine is mainly governed by the pH of a solution and is poor at pH 7. In comparison to leucine, it has better surface activity and poor aqueous (approx. 3-fold) solubility and is amorphous following the SD. Its aqueous solubility and pH-dependent behavior promote the formation of low density highly corrugated particles with reduced inter-particulate interaction and cohesiveness; which eventually can control the solid-state aggregation with improvement in the flowability and dispersibility of powder [26, 77].

3.6 Inhaler Device and Capsule Coating

Various active researchers explored the DPC techniques, FCAs for tailoring the performance of powder and particles. Few formulation scientists initiated the idea of coating inhaler device and capsules with suitable material to improve the dispersion and de-agglomeration performance of DPIs. These interesting cases related to the inhaler device and capsules coating are described here.

Behara *et al.* 2014, studied the effect of CC₁-3Dm inhaler and hydroxypropyl methylcellulose (HPMC) capsule surfaces coating effect on the aerodynamic performance of albuterol sulfate. Device (CC₁-3Dm) and HPMC capsule were carefully coated using lower surface energy material, i.e., polytetrafluoroethylene (PTFE) suspension (LUTM 708, Sprayon Products, OH). Additionally, the HPMC capsule was layered using low surface energy powders, i.e., leucine and MgSt. PTFE coating of the CC₁-3Dm inhaler and HPMC capsule has a considerable impact on capsule shell drug retention, mutually with reducing mouthpiece (MP) and capsule chamber retention related to uncoated inhaler device. PTFE coated CC₁-3Dm inhaler displayed 1.27 and 1.25-fold improvement in emitted dose as related to uncoated resin and metal array device, respectively. PTFE coated CC₁-3Dm inhaler showed 1.45 and 1.12-fold reduction in MP retention than the uncoated resin and metal array device, respectively. Moreover, PTFE coated CC₁-3Dm inhaler also showed a marked 4-fold reduction in capsule chamber retention as related to both uncoated inhalers. Furthermore, PTFE coated HPMC capsules showed a 1.93 and 2.21-fold reduction in capsule retention as compared to capsules actuated from uncoated resin and metal array device, respectively. Coating the capsule shell with the ingredient of lower surface energy also showed a significant impact on the aerosolization performance of albuterol sulfate. Capsule coating with MgSt showed a decrease (1.54-fold) in the capsule shell drug retention as related to the uncoated capsule. However, there was

no considerable variation among capsule shell drug retention for the MgSt and LEU capsule coatings. This shows that the chemical nature of coating material may not perform a crucial function in lessening capsule shell drug retention. In summary, the coating of the inhaler and/or capsule has a major impact on the aerosolization functioning of the drug substance. However, extra efforts are needed to explore the effect of coating materials size and capsule aperture orientation on powder dispersion [82].

In a study by Heng *et al.* (2013), inhalers (i.e., Rotahaler[®] and Aerolizer[®]) and capsules (size 3 HPMC) were coated carefully by ethanol-based MgSt suspensions (0.05, 0.1, and 0.3 g/mL) to improve the overall aerodynamic fate of DPI. Spherical shape, smooth surface spray-dried lysozyme (1.91 μm) particles were used as a model drug. The aerodynamic assessment was performed using a multi-stage liquid impinger (MSLI, Copley, UK) at a flow rate of 60 L/min. Aerolizer[®] device containing coated capsule (0.3 g/mL) showed a maximum reduction in capsule shell retention with a marked 89% powder reduction as compared to the uncoated capsule. In a similar manner, the coated Aerolizer[®] device (0.3 g/mL) exhibited a maximum reduction in device retention and displayed a marked 52% powder reduction as compared to the uncoated device. Coated (0.3 g/mL) Aerolizer[®] device, as well as a capsule, demonstrated a marked 79% and 69% reduction in powder retention as compared to the uncoated counterparts, respectively. Similar to the Aerolizer[®] device, coating (0.3 g/mL) of Rotahaler[®] device and capsules showed a maximum reduction in device and capsule powder retention. Coating (0.3 g/mL) of both the Rotahaler[®] device and capsule showed a marked 73% and 53% reduction in powder retention as compared to their uncoated counterparts, respectively. In both cases, a significant reduction in powder retention was mainly attributed to the ability of MgSt to shape superior Langmuir-type films which impart anti-adherent features to the coated face. MgSt coating is known to reduce the adhesion between the spray-dried lysozyme particles and the interior facade of the capsule shell and device, which sequentially elevates the aerosolization performance [83]. However, a lot of active efforts need to be invested for commercial translation of such coating technologies.

3.7 Numerical Simulation

The primary theory of DPC includes the mixing of guest (drug) particles with host (carrier) particles using a suitable mixing technique [26]. Although this idea is simple, the mechanism involved in DPC is multifaceted and interrelated [84]. The blending of API and carrier particles is

a decisive key process that regulates overall DPI functioning [85]. While interactions between API and carrier particles, for instance, molecular van der Waals forces, Coulombic electrostatic charges, and moisture uptake (capillary action), are prime parameters that conclude how the drug particles adhere and detach from the carrier molecules [26, 86]. Ultimately, drug-carrier interactions and other physiochemical properties (particle size, morphology, interface attributes) of powder blend have an influence on the overall performance of DPIs [86]. Thus, to understand these complex and multifaceted systems, various researchers explored in-silico modeling, i.e., numerical modeling, simulation, and computational fluid dynamics (CFD) experiments. Few interesting case studies related to particle-particle interaction and particle-mixing equipment interactions are described in the succeeding section.

Yang *et al.* (2013) studied the particle adhesion mechanism during powder blending using discrete element method (DEM) analysis. The author showed that the critical sticking velocity and particle radius had a crucial influence on the work of adhesion. While, during mixing, optimal vibration velocity frequency and amplitude are fundamental to maximize the contact number. DEM revealed that the particle sticking potential reduces as the frequency or amplitude is augmented [86]. The same research group also studied the electrostatic interface during particle mixing in DPIs by DEM analysis. The DEM analysis is explored to probe the outcome of electrostatic energy on a DPI wherein API particles and pre-charged carrier particles are blended in a vibrating container. During mixing the pre-charged carriers were found to control the electrostatic interactions between the API and carrier particles while the size (capacity) of the mixing container had a major impact on mixing performance. The mixing efficacy in the electrostatic state is superior to the van der Waals state when the vibrational frequency and amplitude are lower [86]. Similar to these investigations, various flow simulations, fine particle tracking, and multi-scale modeling analysis were performed to understand particle-particle interaction during mixing and ultimately to optimize the DPIs [87]. Modeling-based DPI development is a good policy for exploring its usefulness in decision-making during the optimization of carried-based formulations.

3.8 Conclusion

Dry powder coating is a potential strategy for improving the aerodynamic performance of dry powder inhalers. As summarized in this chapter, dry particle coating, as well as force controlling agents, have shown to be a

feasible approach for the development of versatile particles with improved aerosolization characteristics. A variety of processing techniques and a range of force controlling agents are available for materialize functionalized inhalable powders and particles. Additionally, the dry powder coating practice is a single step as well as easy to scale-up. However, it is well evident that, in the upcoming era, extensive experimental efforts are needed to optimize and understand the in-depth mechanism of eco-friendly dry powder coating technology.

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Superhydrophobic Polymer Coatings

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Abstract

A surface is considered as superhydrophobic in the case of having more than about 150° the apparent contact angle and hysteresis and sliding contact angles less than 10° and 5° , respectively. In addition, it must have a good physical and mechanical stability. Many of artificial hydrophobic polymer coatings are prepared by nature inspiration like lotus leaf. Furthermore, the superhydrophobic coatings with additional functions have recently been developed in various fields of applications such as anti-icing, self-cleaning, water repelling, and anticorrosion coatings. The aim of this chapter is reviewed briefly the important parameters for preparation of superhydrophobic coatings, working mechanisms, as well as fundamental models of superhydrophobicity.

Keywords: Superhydrophobic, models, surface tension, self-cleaning, coatings application

Abbreviations

r	Parameter related to Surface roughness
φ_n	Surface fraction related to material of n
θ and θ_x	Contact angle is usually used for water and x is a specific index from the following list:
γ	index of Young equation
w	index of Wenzel model
c	index of Cassie–Baxter Model
h	Hysteresis

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θ_a	Advancing contact angle on a sloping surface (at the lower side)
θ_r	Receding contact angle on a sloping surface (at the upper Side)
γ_z	Surface tension and z is a specific index from the following list:
γ_{SG}	Properties at the solid-gas interface
γ_{SL}	Properties at the solid-liquid interface
γ_{LG}	Properties at the liquid-gas interface
γ_{LV}	Properties at the liquid-vapor interface
g	the gravitational constant
$\Delta\rho$	the mass density difference of the fluids
λ_c	capillary length

4.1 Introduction

Many scientific technologies are bioinspired, and among them, superhydrophobic coatings in the field of surface technologies led to a series of innovations and new applied researches [1–3]. Hydrophobic coatings are used for different applications to conserve of historical monuments, self-cleaning for window glasses and clothing articles, anti-icing for outdoor applications such as automotive and airplane, etc. The innovation of superhydrophobic coating and research papers are progressively improved. Figure 4.1 indicates the number of articles in superhydrophobic topic from Google Scholar Web. As it seen from the presented data in this figure, the research articles indicate about 10 times growth in hydrophobic coatings topic during two decades.

Nature has always been a human inspiration in the development of science and technology. Many interdisciplinary researches are based on this background (see Table 4.1). Superhydrophobic materials are among the most prominent examples from nature in surface research and physical chemistry of the surface interface. The development of superhydrophobic materials has led to a number of new research innovations applied across a wide range of fields.

4.2 Theoretical Background

A shape of suspended liquid drop is specified by resultant of two forces, i.e., the surface tension ($\gamma_{lv} \times d$) and gravity ($\rho g d^3$). The first one creates a spherical form to minimize surface area. However, the latter attempts to

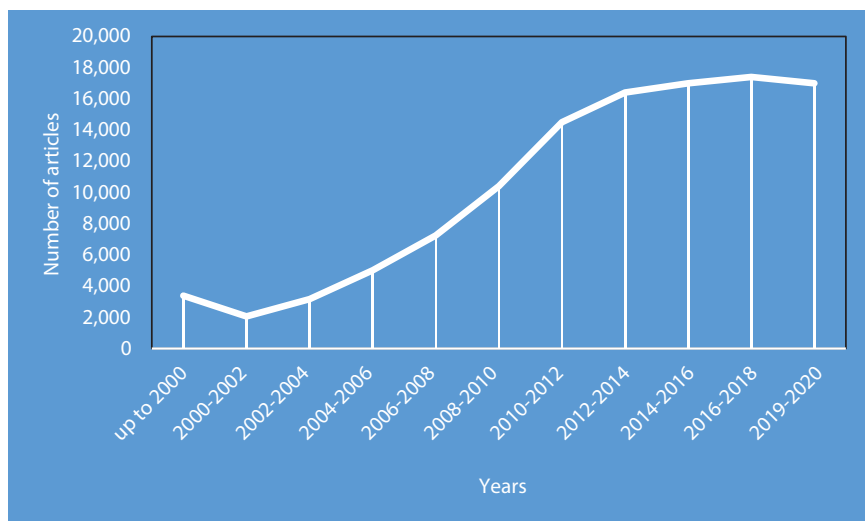


Figure 4.1 An increase trend of the number of research papers with title of superhydrophobic coating in the past two decades.

Table 4.1 Some characteristics of natural examples of hydrophobic surface [4].

Lotus leaves	Low drag and adhesion
Rice leaves	Anisotropic wettability and low adhesion
Butterfly wings	Low and directional adhesion
Gecko feet	High adhesion
Red rose petals	High adhesion
Snail shell	Oleophilic

flatten the drop. The effect of the size of drop on its shape is determined by comparing it with the capillary length.

The capillary length or capillary constant is a fundamental physical property that balances gravity (body forces) and surface tension (Laplace pressure). The capillary length depends on type of liquids and ambient conditions [5, 6].

In the case of a liquid drop immersed in another fluid (e.g., air), the capillary length denoted λ_c is given by.

$$\lambda_c = \sqrt{\frac{\gamma_{LV}}{\Delta\rho \cdot g}}$$

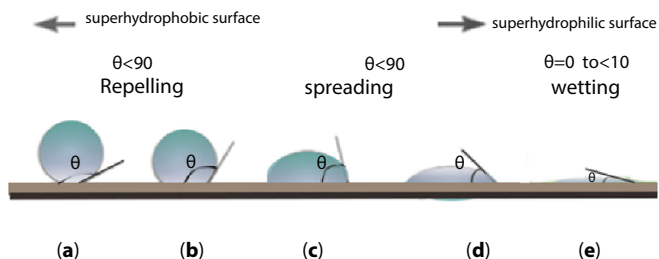


Figure 4.2 Schematic presentation of water droplet on the rigid surface: (a) super hydrophobic, (b) hydrophobic, (c) and (d) hydrophilic, (e) super hydrophilic.

The liquid drop is considered small when its diameter is smaller than the capillary constant. The capillary length is about 3 mm (2.71 mm) for drop water in air at room temperature (20°C) on Earth [7, 8].

The surface hydrophobicity can be measured by placing of a small liquid droplet (e.g., water droplet) on a rigid surface in an equilibrium state. Figure 4.2 shows schematically four categories of the rigid surfaces based on the water contact angle measurement: (1) superhydrophobic, the contact angle (θ) is more than 150° , (2) hydrophobic when θ is in the range of less than 150° to 90° , (3) hydrophilic when θ is less than 90° up to 10° , and (4) superhydrophilic when the contact angle (θ) is less than 10° and near zero degree [9].

The contact angle measurement is based on the surface substrate condition like as smooth or roughness, homogenous, and the fluid surrounding conditions such as temperature.

The Leidenfrost effect describes the hot solid surface that makes a water vapor film when the water drops deposit on it. In this case, the surface indicated the apparent water contact angle at about 180° with a hysteresis contact angle in the range of 0° [3, 10].

4.2.1 Young's Equation

Thomas Young formulated an equation, called “Young’s equation” based on the shape of a liquid drop on the solid surface for quantification of

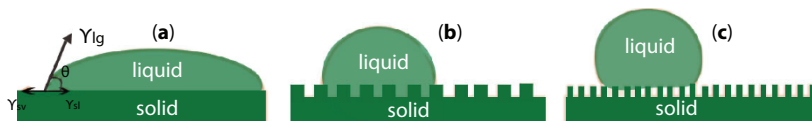


Figure 4.3 Schematic image of a liquid drop on the surface by different models: (a) Young, (b) Wenzel, and (c) Cassie-Baxter.

wettability [11]. When the small liquid drop is set on a flat homogenous rigid and horizontal surface where θ represents the liquid contact angle as seen in Figure 4.3a, three surface tension interfaces become a predominant factor: surface, liquid, and vapor. “Young’s equation” establish a relationship between three interfacial surface tensions (i.e., solid-vapor, solid-liquid, and liquid-gas or vapor) as

$$\cos\theta_Y = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lg}}, \quad (4.1)$$

where θ_Y , γ_{lg} , γ_{sl} , and γ_{sv} represent the contact angle (by Young model), the surface tensions in the following interfaces: liquid-gas, solid-liquid, and solid-vapor, as seen in Figure 4.3a.

The level of surface hydrophobicity can be determined from Young’s contact angle (θ_Y) and it can be considered as a characteristic of the surface substance [12]. However, the surface roughness is not seen in calculating the young’s contact angle by this equation [13].

4.2.2 Wenzel Model

The Young’s equation is modified by Wenzel model [14]. In this model, the roughness of solid surface is considered while the liquid droplets fill the rough channels on the surface as seen in Figure 4.3b.

Wenzel equation relates the apparent contact angle to the surface roughness as given in Equation (4.2):

$$\cos\theta_w = r \times \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lg}} = r \cos\theta_Y, \quad (4.2)$$

where r is surface roughness as the ratio of actual to geometric surface area and θ_w is the apparent contact angle in this model, respectively.

According to this expression, the roughness of solid surface slightly increases in two interfacial surface tensions (i.e., γ_{sv} and γ_{sl}). Therefore, if the apparent contact angle calculates by Wenzel’s model, it is usually more than the contact angle obtained by Young’s model. Therefore, a hydrophobic solid surface may be considered as super-hydrophobic if roughness is considered [3, 15].

However, the calculated contact angle in the Wenzel model will be more than it from Young’s equation, the droplet movement is more difficult.

It can be attributed to high surface contact of liquid droplet without considering the air (vapor) in the voids (i.e., high adhesion).

4.2.3 Cassie-Baxter Model

Cassie and Baxter expanded the Wenzel's equation by considering the shape of the droplet with increasing surface roughness so that the air (vapor) fills the surface cavities. In this case, droplet cannot enter the cavities and it is in contact with the peak of surface roughness as seen in Figure 4.3c [16].

In this case, a part of liquid droplet connects with the peaks and creates an interface in solid surface and liquid droplet while the rest of liquid droplet touches with the vapor or gas in the cavities. This part of liquid droplet makes an interface between the liquid and vapor or gas in the cavities. Therefore, the apparent contact angle, θ_c in Cassie-Baxter's model can be calculated as following:

$$\cos\theta_c = \varphi_1 \cdot \cos\theta_Y - \varphi_2 = \varphi_1 \cdot \cos\theta_Y - 1 + \varphi_1, \quad (4.3)$$

where φ_1 represents fraction of air (i.e., gas or vapor) in the voids and φ_2 is fraction of solid surface [17, 18].

In this model, the liquid droplets only touch the tip of surface peaks and rolling off from the substrate's surface in a low sliding contact angle (i.e., it is the minimum angle at which a liquid droplet begins to roll down in a sloping surface). From this point of view, the sliding angle is also an essential factor besides the apparent contact angle, for evaluation of surface hydrophobicity [19].

In this regard, the surfaces have a high contact angle and may be don't have a low sliding angle. A phenomenon is seen in the red rose petals by a high surface roughness in nano size and also a surface with high hydrophobicity. The water droplets cannot roll off from the inclined surface because of the high adhesion forces [20].

In addition, the hysteresis contact angle (θ_h) is another important parameter in surface hydrophobicity. The droplet makes an asymmetrical shape on a sloping surface with two contact angles: advancing (θ_a) at the lower side and receding (θ_r) at the upper Side. The difference between these two contact angles is called as the hysteresis contact angle [21–23].

Therefore, it is necessary for creating a super hydrophobic surface, the coating possess a high apparent contact angle, and the low hysteresis contact angle.

Another important parameter in the preparation of super hydrophobic coating is surface morphology, which may have different microstructures containing various combinations of nano and/or mico levels on a

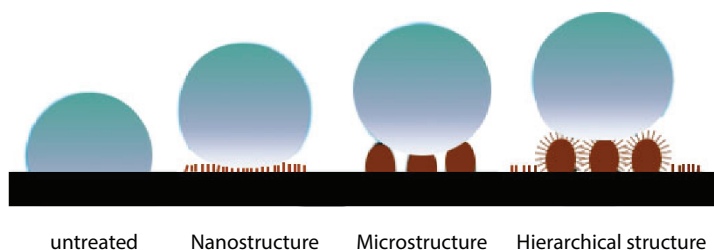


Figure 4.4 The effect of surface microstructure on changing hydrophobic to superhydrophobic behavior.

rough surface (see Figure 4.4). One study found that the effect of surface roughness was not as effective as its chemical nature on hysteresis [24]. In another study, it has been attempted to distinguish between the advancing contact angle (θ_a) and the droplet mobility [25].

4.3 Physical and Chemical Texturing

Physical texturing is an essential process for eliminating surface imperfections, impurities, and surface oxides especially from metallic surfaces. This process may require chemical texturing with coating techniques to enhance surface topography. Some coating methods for metallic surfaces are mentioned in the following.

4.3.1 Cleaning Process

The first step of any coating process is the surface cleaning. It is essential for eliminating of contaminants and getting durability, uniformity, and reproducibility [26]. In addition, it is advisable in most cases to coat immediately after cleaning the surface. The cleaning processes established in literature can be classified as follows: (1) wet chemical procedures use different mixes of organic solvents, acidic and/or bases solutions at various conditional variables such as times, strengths and temperatures. (2) Dry methods; this category can be pointed to, for example, (Ar or O₂) plasma, laser, UV-ozone, pyrolysis treatments. Furthermore, mechanical process can be considered as a pre-cleaning step.

4.3.2 Wet Chemical Reaction

One of the popular methods to increase hydrophobicity of surface is wet chemical etching in the presence of suitable chemical agents and ultrasonic

waves. It forms a superhydrophobic surface by creating nano and/or micro structures morphology [27].

4.3.3 Sol-Gel Process

Modified and functionalized silanes and alkoxy silanes can be applied on a wide range of substrates such as ceramics, metals, glass, by using sol-gel processes in different techniques like dip coating, spin coating, to create a superhydrophobic surface with silica nanostructured lattices [28].

4.3.4 Immersion Coated

The reagents are used effectively and the test time is shorter in this method. By etching and using hydrophobic precursors such as 1H, 1H, 2H 2H per fluoro decyl triethoxysilane, it is possible to create uniform micro-nanostructures with superhydrophobic properties [29].

Furthermore, it is reported that superhydrophobic and self-cleaning coatings were prepared on aluminum surface by an acidic etching (HCl and HNO_3) then treated with lauric acid [30].

4.3.5 Electrochemical Deposition

The superhydrophobic surfaces were prepared on copper metal surface by electrochemical deposition in dilute ethanolic stearic acid solution and by direct current. The surfaces had water contact angles of 153° and hysteresis of 2° [31]. This superhydrophobic property is attributed to the small-scale nanoporous microstructure of surface and also a hydrophobic copolymer coated on this morphology by CVD electrochemical deposition.

4.3.6 Ion Irradiation or Implantation

High-energy ions can play a key role in surface modification, depending on the ions and its types. Surface hydrophobic modification can be accomplished by ion implants with low-energy ions up to several hundred kV. In this method, the interaction of ions with substances and ions at the material level is the determining factor in hydrophobicity and superhydrophobicity. The type of ion beams used, for example, argon or nitrogen, affects the composition of the surface and changes its roughness. The effects of

ion beam irradiation on ultra-hydrophilic films showed that the material morphology could change to hydrophobic in nature [32, 33].

4.3.7 Plasma Treatment

Plasma treatment generally uses ionized gas, which is created by the use of excess energy on the gas. This energy can be used to etch and clean the surface, to fabricate surface nanoparticles and also create nano and micro roughness [30, 31]. In addition, these operations can be applied at low temperature for surface modification of polymers, for example, polystyrene (PS) substrates. Plasma treatment has been performed on copper joints to prevent corrosion in these materials. By plasma etching on copper surfaces with functionalized fluorinated compound, a hydrophobic coating with micro/nano roughness was created which showed WCA as high as 163° and a low θ_h at about 1° (see Figure 4.5) [34, 35].

Recently, all types of hydrophobic and anti-reflex coatings on glass have been reviewed. According to this paper, hydrophobic coatings comprise the main categories:

1. Plasma surface treatment,
2. Sol-gel process,
3. DC sputtering.

Though among them, the sol-gel method, including effective parameters, solvent and precursor selection, and limitations, has been emphasized. On the other hand, this type of coating is also applied to anti-reflection (AR) coatings through the sol-gel method. Furthermore, the challenges of this method, including delicate cleaning methods and water-based hydrophobic coatings, which are suitable for biological and eye-contact applications, have also been investigated [26].

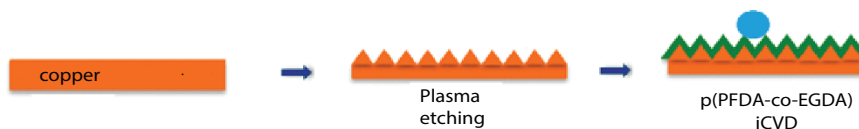


Figure 4.5 The micro and nano roughness is created on the metallic substrate by O_2 -Ar-plasma etchings for fabrication of low surface energy. In the following step, a hydrophobic copolymer, containing 1H, 1H, 2H, 2H perfluoro decyl acrylate (PFDA) - ethylene glycol diacrylate (EGDTA) was coated on the etched metallic surface via initiated CVD [35].

4.4 Development of Superhydrophobic Coatings With Nanoparticles

The use of nanoparticles is one of the common ways for the preparation of superhydrophobic coatings. In this section, some of recent progress will be introduced in this field as well as the fabrication methods [36].

4.4.1 CNT Nanoparticles

A simple and effective way for constructing superhydrophobic hybrid membranes is proposed through the covalent bonding of the hydrophobic polymers such as polystyrene to the modified carbon nanotube. The membranes have fire-retardant properties and high performance in oil/water separation.

The methodology for manufacturing superhydrophobic polymer/CNTs hybrid membranes is surface modification of CNTs by creating some photocatalytic modifications, -COOH and -OH groups on carbon nanoparticle surfaces which can be followed by grafting a typical hydrophobic polymer brushes, for example, PS in a photo-polymerization process. The superhydrophobic hybrid membranes can separate water from oil emulsions with a wide range of absorption and good recycling [37].

Recently, thermomechanical properties of super hydrophobic coatings have been investigated. The thermal cycling was applied on the multi-walled carbon nanotube and silicone nanocomposite coatings. Stress relaxation and wetting properties of silicone and multi-walled carbon nanotube (MWNT) nanocomposite were studied. Super hydrophobic coating for anti-frosting applications is used for energy conservation and safety reasons. Safety factor is a critical parameter which may be concerned in cold weathering regions by wide fluctuation of daily temperature. However, the thermomechanical cycling which can be supported by the superhydrophobic and anti-icing coatings should be quantitatively studied under stress relaxation and wetting behavior.

The silicone - MWNT nanocomposite coatings indicated a microstructure with a lot of open nanopores between the nanoparticles explained as the Cassie-Baxter model. In addition, a superhydrophobic coating should be an adjustment of thermal expansion coefficient by the substrate to avoid of thermal stress.

It has been reported that the amount of stress relaxation for the open microstructure of silicone -30% MWNT nanocomposite reaches about 80% of the value for its same composite with a closed and non-porous

microstructure. In addition, the structure and composition of the superhydrophobic silicone - MWNT coating are important fabrication parameters that should be controlled to withstand a lot of thermal cycles. Furthermore, the nucleation and growth of ice crystal can be delayed by size and shape of nanoparticles in anti-icing and hydrophobic coatings [38].

4.4.2 Carbon-Based Fillers

Nano graphene and graphene oxide have been considered for its good electrical properties, thermal conductivity, simple, and inexpensive synthesis methods just as probability to apply them for synthesizing of various types of nanoscale materials, especially super-hydrophobic, anti-corrosion, and anti-microbial coatings. The preparation of stable dispersed nanoparticles in various interfaces such as liquid-liquid and air-liquid interfaces and dual functional agents is the important factors in the preparation of this kind of coatings [39].

Graphene and carbon nanotubes can be used for superhydrophobic coatings due to their nonpolar structure and inherently high surface area. The study exhibited that modification of graphene aerogels with a silane coupling agent induces superhydrophobicity. Furthermore, the amount of modified graphene aerogels was investigated on the receding water contact angle. The results indicated that graphene aerogels are hydrophobic. In addition, a fluorinated treatment can be induced an increment in superhydrophobic property. The result also indicated the modified graphene aerogels compare with the carbon nanomaterials generate higher superhydrophobic property. Moreover, the synthesize procedure is capable to produce in scale up production. It was shown that the hydrophobicity of coating can be improved by modification of graphene's surface with 1H, 1H, 2H, 2H per fluoro decyl tri chlorosilane (FDTS). The results indicated the contact angle can increase from about 125° for unmodified graphene to 160° where it is modified [40].

4.4.3 Silica-Based Superhydrophobic Nanocoatings

Anti-icing coating is an important application of ultra-hydrophobic material. This kind of coating can be used in aircrafts, ships, refrigerators, wind turbines, etc [41, 42].

All hydrophobic coatings are not anti-icing. However, the formation of ice can be delayed at the presence of hydrophobic surfaces. Furthermore, the microstructure of surface and consequently their superhydrophobic

properties can be severely reduced by repeating the freeze-thawing cycle [43–45].

A series of nanocomposites were fabricated as anti-icing coating based on organic modification of silanes as a coupling agent and silica nano particles in a range of 20 nm up to 20 μm with cross-linked the acrylic polymers. The result indicates that the surface-modified silica particles have an inherent water contact angle about 110° . In addition, all of the nanocomposite coatings except it containing 20 μm silica particles possessed the superhydrophobic properties with the water contact angles more than 150° and the hysteresis contact angle less than 2° by a maximum in superhydrophobicity for sample containing 50 nm silica particles. It can be emphasized that the critical size of silica nano particles on the coated surface are among of important parameters in the anti-icing properties as well as their superhydrophobicity but in two various length ranges. The probability of icing indicates an increasing curve as a function of silica particle size. It can be described by a heterogeneous nucleation model. Therefore, any superhydrophobic coating is not necessarily an anti-icing surface and it is important to achieve these dual properties by designing the surface morphology and tuning surface textures in various length scales [46].

4.5 Transparent Superhydrophobic Coatings for Self-Cleaning Applications

The self-cleaning surface can be formulated in two main ways: in the first process by combining a super-hydrophilic and photocatalyst coating or in the second way by a combination of super-hydrophobic and photocatalyst coating [47–49].

The presence of photocatalytic nanoparticles such as titanium dioxide nanoparticles with anatase structure on the superhydrophobic surface can decompose contaminants and impurities of organic origin and the water flow or raindrops washed away the decomposed particles and dusts by formation of a film of water in a superhydrophilic surface or the rolling effect in a superhydrophobic coating (see Figure 4.6) [50–53].

Therefore, the use of transparent self-cleaning coatings can prevent dirt build-up on the surface and increase surface efficiency for various applications such as solar panels, tiles in the bathroom, glass industries for various applications like building window and automotive glass, architectural protection, and monument conservation, etc [36, 54, 55].

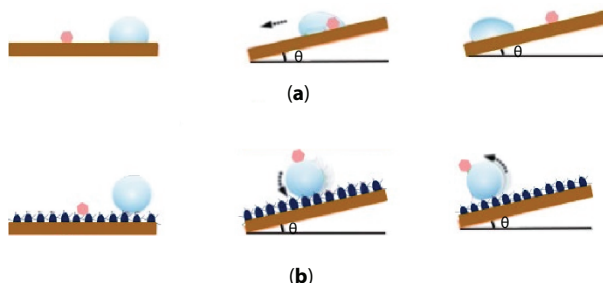


Figure 4.6 Schematic presentation of self-cleaning surface: (a) normal and (b) superhydrophobic (the water drops roll over the slipped surface and clean it from the decomposed organic dirt).

4.6 Superhydrophobic Coatings With Additional Self-Cleaning Function

Superhydrophobic coatings with additional self-cleaning function may be divided into four general categories.

4.6.1 Nanoparticles in Coating

Titanium dioxide nanoparticles in anatase or rutile structures are common materials for preparation of self-cleaning coatings due to its unique physical stability and photocatalytic activity for self-degradation of organic containments [56, 57].

4.6.2 Plant Leaves

Many plant leaves and the most prominent of them, the lotus leaf, are hydrophobic and self-cleaning with a small sliding angle, which is the source of much scientific and industrial research. Lotus effect is known as the intrinsic hydrophobic effect from epicuticular wax as well as isotropic dual roughness of surface in micro and nano ranges [58, 59].

4.6.3 Animal (Gecko Setae)-Inspired

A few animals in nature, such as Gecko and crawlies, have an extraordinary ability to attach and detach from the surface. The extraordinary adhesion of Gecko foots is ascribed to millions microscopic arrays of well-aligned

leg hair having about 110 μm length and 5 μm diameter that come apart many of smaller nano range (200–500 nm) ends named spatula [60, 61]. However, the toes are highly hydrophobic but they can adhere strongly to both hydrophilic and hydrophobic surface whatever the polarity of surface chemistry. The high adhesion is attributed to Van der Waals force instead of surface polarity [62–65].

4.6.4 Marine Organisms-Inspired Antifouling Self-Cleaning

The recent researches on polymer-based marine biofouling coatings, for example, skins of shark and whale are reviewed in literature. Based on this study, the adhesion behavior is an important parameter in synthesis of polymeric coating for anti biofouling in marine applications [58, 66, 67].

Recently, the role of the surface topography of the particle contact area and its adhesion has been investigated. The geometry of the surface perturbation affects the contact area and the particle anisotropy on this surface. The local stiffness can be affected by surface topography which determines the strength of adhesion. In this study, topographic features of the surface have been studied systematically and each of them is discussed on the desirable surface and nature of adhesion in the design of corrugated topographic surfaces [64].

4.7 Summary and Outlook

Superhydrophobic surfaces with special features and additional functionalities like self-cleaning, antibacterial, corrosion-resistant, anti-stain, anti-pollution, snow-paste, dust-proof, and many more functionalities are widely used in different industries.

Extensive research is underway to build hydrophobic surfaces and coatings inspired by nature-based materials. Examples of the nature and understanding of their mechanisms and theoretical models provide scientists with an interest and challenge to develop durable superhydrophobic surfaces with nanosynthetic processes by surface modification by chemical and physical methods. However, despite the numerous methods proposed for the manufacture of superhydrophobic surfaces, the mechanical strength and durability of such surfaces for various applications remains a major challenge. Because the superhydrophobic property of these surfaces depends on the exterior area and if it is damaged or wiped out, the surface hydrophobicity disappears, so the challenge is to build volumetric

hydrophobic materials that their bulk has superhydrophobic property. In this case, it can exhibit durable superhydrophobicity without considering eventual surface damage. Hydrophobic surfaces in the next generation should be multipurpose. The hydrophobicity is combine with additional functions, like transparency, superelophobic, self-cleaning, de-icing, disinfection, and low-cost coating. Further studies should be conducted towards scale up manufacturing processes using cheaper, environmentally friendly raw materials to prepare them for wider industrial applications.

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Superhydrophobic Coatings Applications

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Abstract

The superhydrophobic coatings have various applications that determined by the substrate, the molecular structure of the coating, and the environmental conditions. The final properties of the coatings depend on the physicochemical characteristics of the substrate and coating. According to the substrate and coating properties, the application of the superhydrophobic coating were determined. Therefore, in first step, substrate and molecular structure of the superhydrophobic coatings were investigated. Afterwards, in the second step, application of these coatings is divided into the three major group and examined.

Keywords: Superhydrophobic, repellent, surface tension, self-cleaning, coatings application

5.1 Introduction

In order to investigate the application of superhydrophobic coatings, two steps were examined. The first step is the study about the nature of the superhydrophobic coatings and substrates. The second step focused on the study about superhydrophobic coatings applications which originate from physicochemical characteristics of the coatings and substrates. In first step, physicochemical characteristics of the substrates and coatings as two significant issues were examined. This step has significant role to understand the nature of the superhydrophobic coatings which determine the properties and application of the superhydrophobic coatings in different situations. The first part investigates the nature of the substrate and coating divided

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into two subsets which include study about substrates and superhydrophobic coatings, respectively. The final application of the superhydrophobic coatings was determined according to the physical and chemical properties of the substrate and coatings which are showed in Figure 5.1.

The first significant issue in the first step is the substrate characteristics. Different types of substances are used as substrates including building materials [1–4] (especially brick-like substances) [5–7], Coating [8–10], glass [11–15], leather [16], metal [17] (especially steel) [18–21], paper [22–25], plastics [26–28], solar cell [29–32], textiles [33–37] (especially cotton) [38–41], and wood [8, 42–44] were investigated. The substrates physicochemical characteristics have significant influence on the choice of the coatings type. The substrate roughness [45] and the polar bonds content [46] in substrate are the two major subject in physicochemical characteristics of substrates. The second issue in the first step is about nature of Superhydrophobic coatings and their chemical structure. Superhydrophobic attribute exists in some organic and inorganic substances which originates from very low surface tension of these substances [47, 48]. The two significant issues in

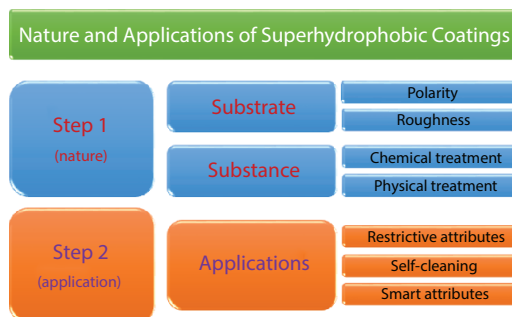


Figure 5.1 Investigation of the superhydrophobic coatings applications in two steps.

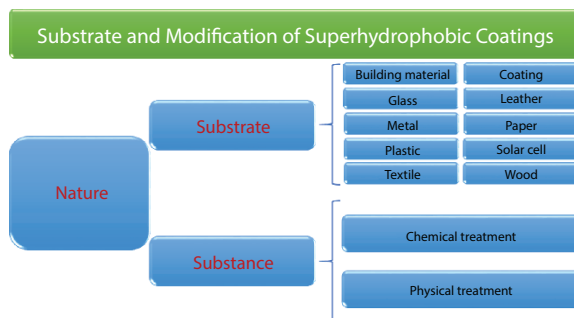


Figure 5.2 Superhydrophobic coatings substrates and substances.

the first step were showed in the Figure 5.2. After reviewing these two significant issues in the first step (nature of materials), the coatings could be classified according to their application into the three main group.

5.2 Step I

The coating and substrate characterization have significant influence in different applications like superhydrophobic coatings applications. Therefore, physical and chemical properties of the substrate and coating must be investigated in the first step.

5.2.1 Substrate

Roughness is the most important factor in the physical properties of the substrate. Roughness growth in the nanoscale could lead to the form superhydrophobic in the surfaces [18]. Also, chemical structure of substrate determined interactions between substrate and coating. Substrate roughness and substrate chemical bonds are two important properties have influence on the coating adhesion and durability which determines the type of coating [49, 50]. Not only the substrate roughness is affected on the coatings adhesion but also the roughness of the coating effects on the properties of the superhydrophobic coating [51, 52].

5.2.2 Substance

Superhydrophobic attribute could produce by chemical and physical techniques. However, the chemical methods have more variety than the physical methods. The chemical methods include organic and inorganic substances. Various organic and inorganic substances have the ability to produce superhydrophobic property on the surface which are showed in Figure 5.3. Organic substances in four group and inorganic substances in three group could produce superhydrophobic property on the surface. Organic materials are long chain hydrocarbons, organofluorine, organosilicon, and organic aerogel. The inorganic materials are inorganic aerogels, inorganic nanoparticles and nanowires. The long chain hydrocarbons are lauric acid [9, 53], stearic acid [54], glycerol stearoyl ester [42], octadecyl isocyanate [55], Octadecyl mercaptan [56], n-Octadecylamine [57], and myristic acid [58]. Cellulose aerogels [57, 59] and carbonaceous aerogel [60] as organic aerogels are the last group of superhydrophobic organic substances. The organofluorine compounds including water-dispersed perfluorinated

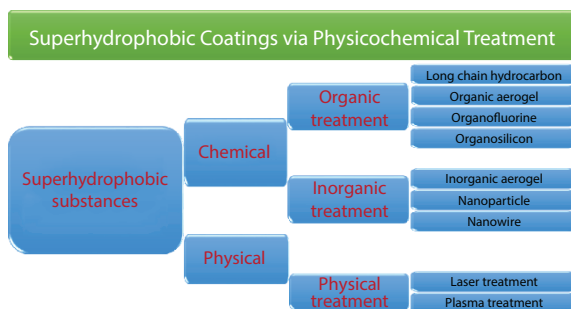


Figure 5.3 Superhydrophobic approach via chemical and physical techniques.

acrylic copolymer [61], 1H,1H,2H,2H-perfluorodecanethiol [36, 41], 1H,1H,2H,2H-Perfluorooctyltriethoxysilane [20, 21, 60], Fluorinated ethylene propylene [31], 1H,1H,2H,2H-perfluorodecyltrichlorosilane [62], 1H,1H,1H,2H-perfluorodecyl trimethoxysilane [63], Polytetrafluoroethylene [35], Perfluoroalkyl methacrylic copolymer [44], poly(2-perfluorooctylethyl methacrylate) [64], and Heptadecafluoro-1,1,2,2-tetra-hydrodecyl-trichlorosilane [17, 65].

Also, the organosilicon substances are methyltrichlorosilane [37], Polydimethylsiloxane [15, 66, 67], Tetraethyl orthosilicate [15], Hexadecyltrimethoxysilane [68], Hexamethyldisilazane [29, 69], (3-Glycidyloxypropyl) trimethoxysilane [29], chlorotrimethylsilane [70], polyhedral oligomeric silsesquioxane-graphene oxide [71], Hexadecyltrimethoxysilane [72], and Heptaisobutyl-Polyhedral oligomeric silsesquioxane-propyl methacrylate [73]. Superhydrophobic inorganic materials were divided into the three major group. Silica aerogels [74] as inorganic aerogels were used to produce superhydrophobic property in different studies. Also, nanosilica [10, 75–77], Gold (III) chloride tetrahydrate (HAuCl_4) [78], and silver(I) oxide (Ag_2O) [79] nanosilver [36] were used as inorganic nanoparticles. Finally, Copper hydroxide nanowires [80], Copper Nanowire [80], ZnO nanowires [58, 77], carbon nano fiber silicone nanofilament [27, 81], and $\gamma\text{-Al}_2\text{O}_3$ [82] as nanowires. The physical techniques through roughness surface alteration were produced superhydrophobic surfaces including laser [18, 83, 84] and plasma [85, 86] treatment.

5.3 Step II

The coatings application categorized into the three main parts: self-cleaning, restrictive attributes, and smart attributes that are showed in

Figures 5.4 and 5.5. Self-cleaning is referred to the spontaneous decontamination of the surfaces against different liquid and solid pollutants. In other words, self-cleaning properties prevent sticking various types of materials on the surface. In order to approach self-cleaning superhydrophobic attribute, the contact angle between surface and pollutant must be increased that lead to decrease adhesion between pollutant and the surface. The restrictive attributes refer to some properties which prevent to occur some unfavorable events on the surface like fungal growth or corrosion beginning. Preventing such undesirable issues have great importance because these unfavorable events cause significant financial loss to the industries around the world. The smart attributes refer to some properties which could change in different situations like self-healing, self-assembly, and stimuli responsive properties. All superhydrophobic applications were examined in this section.

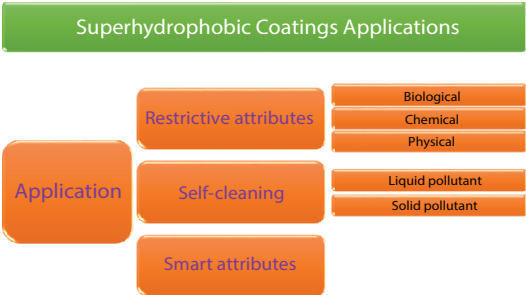


Figure 5.4 Superhydrophobic coatings applications.

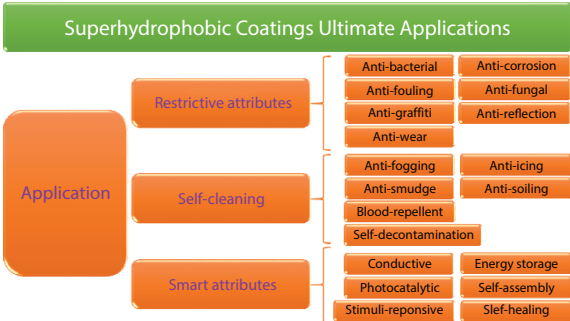


Figure 5.5 Superhydrophobic coatings application in different situations.

5.3.1 Restrictive Attributes

The adhesion of various materials on the surface could make other negative secondary phenomena in addition to the dirt and unpleasant appearance which showed in Figure 5.6. One of the most important of these undesirable phenomena is the corrosion that annually causes immense financial losses to the industry. The surface superhydrophobic attribute could prevent the materials adhering on the surface and consequently prevent these undesirable properties.

5.3.1.1 Biological Agents

Living organisms can stick to the surface and lead to surface contamination. Also, it can lead to other inappropriate issues such as surface corrosion. Therefore, it is important to prevent the living organism's adhesion to the surface. Mainly, organisms that can adhere to the surface are divided into macro and nano scales. The macro scale includes moss, and also the nano scale includes algae, bacteria, and fungi.

5.3.1.1.1 Anti-Bacterial

The bacteria attachment on the surface in addition to reduce surface efficiency can lead to some unpleasant events such as corrosion [87, 88]. Also, bacteria presence on the surface causes various infections and diseases. Therefore, preparation of surfaces which can repel or destroy bacteria has significant importance. The superhydrophobic anti-bacterial surfaces have been prepared via different chemical treatment including tannic acid treatment by silver nanoparticles [36], modification of silver nanoparticles through chitosan and 1H,1H,2H,2H-perfluorodecanethiol [41],

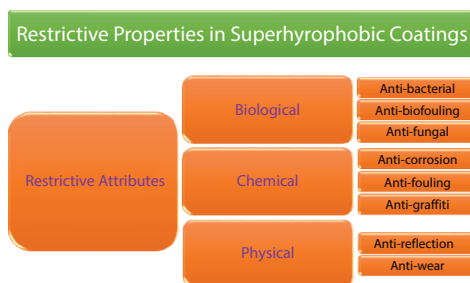


Figure 5.6 Superhydrophobic coatings applications to prevent inappropriate phenomenon.

polydimethylsiloxane treatment by copper nanowires [80], and also zinc oxide nanoparticles treatment by (3-Aminopropyl)triethoxysilane and hexadecyltrimethoxysilane [68]. Applying these coatings in addition to have self-cleaning superhydrophobic feature will also reduce disease and infection probability.

5.3.1.1.2 Anti-Biofouling

Fouling is usually has been originated from other surface phenomena which occurs on the surface. The fouling phenomenon lead to reduce surface efficiency and even corrosion and degradation of surfaces. The fouling materials include living organisms (biofouling like algae [89]) and non-living substance (organic and inorganic) [90] that biofouling is discussed in this section. The non-living fouling will be discussed in the chemical agents. The anti-biofouling feature through superhydrophobic surfaces was obtained. Different substances such as P25 TiO₂ nanoparticles coated with 1H,1H,2H,2H-perfluorooctyltriethoxysilane [91], Cu-electrodeposited Stainless Steel surface via electrodeposition oxidation and vapor deposition [92], elastomeric silicone/graphene oxide γ -Al₂O₃ hybrid nanorods [82], poly(dimethylsiloxane)-poly(tert-butylacrylate)-poly(methacrylolsobutyl POSS) [73], and Sepiolite coated with cinnamic acid and myristic acid have been used to prepare superhydrophobic anti-biofouling coatings [93].

5.3.1.1.3 Anti-Fungal

The fungi attachment on the surface like bacteria organism lead to reduce surface efficiency and some unpleasant events such as corrosion [94, 95]. The chemical treatment of wood by cellulose stearoyl esters and glycerol stearoyl esters [42] and also surface treatment of braze aluminium by heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane were obtained the superhydrophobic anti-fungal surfaces.

5.3.1.2 Chemical Agents

Chemical pollutants cause various types of pollution, reduce performance, and even destroy in different surfaces. In general, the corrosion phenomenon is recognized as the most important issue in surface-limiting substances. There are many parameters contributing to the corrosion phenomenon. Also, the graffiti and adhesion of various non-living substances to the surface are classified as chemical pollutants.

5.3.1.2.1 Anti-Corrosion

The corrosion phenomenon is one of the most important challenges that human beings face. This phenomenon has many different types and various parameters affect in corrosion. Corrosion damages billions of dollars every year to industries of all countries. Therefore, the corrosion phenomenon investigation has been always interested to scientists and industries. The non-adhering to the surface is an ideal idea to prevent the initiation and propagation of corrosion [96]. Hence, superhydrophobic coatings and surfaces are special choice between corrosion inhibitors. There are widespread researches that have been done to prepare corrosion immunity through superhydrophobicity. The anti-corrosion feature through superhydrophobicity has obtained using various chemical treatment such as polyhedral oligomeric silsesquioxane-graphene oxide [71], Zn-Ni-Co coating modification with myristic acid [58], high density polyethylene solution [14], steel modified by 1H,1H,2H,2H-perfluoroalkyltriethoxysilane [20], Polysulfone treated by carbon nanotubes [97], Polydimethylsiloxane [98], zinc treated by NH_4F [99], rubber modified with 1H,1H,2H,2H-perfluorodecanethiol [100], discotic columnar liquid crystals [101], paper treated by hydrophobic fumed silica and carbon nanotube [102], and also covering nylon mesh [103] as physical treatment have been investigated.

5.3.1.2.2 Anti-Fouling

The adhesion and interaction of various organic and inorganic compounds with the surface lead to widespread problems. Therefore, the superhydrophobicity feature can prevent these phenomena [90]. Zinc nanoparticles modified by stearic acid [104] and SiO_2 modified by 1H,1H,2H,2H-perfluorodecyltriethoxysilane lead to prepare superhydrophobic anti-fouling coatings [105].

5.3.1.2.3 Anti-Graffiti

The graffiti especially as vandalism is an important issue that has received serious attention in recent years. This type of contamination has considerable removing cost and also scientists investigate different methods to prevent graffiti contamination. The aluminium coated by Polysilazane-based coatings have hydrophobicity and anti-graffiti feature [106]. Also, the hydroxyl-terminated hyper-branched polyester coating precursor treated by mono-hydroxyl-terminated polydimethylsiloxane obtained hydrophobic anti-graffiti coating. Although obtaining anti-graffiti via superhydrophobic coatings has not been investigated completely but the contact angle

analyses of these two researches were determine more than 100° which means hydrophobicity increase anti-graffiti feature.

5.3.1.3 *Physical Agents*

The anti-reflective and anti-wear properties recognized as physical features which have been obtained through surfaces superhydrophobicity. The variability of physical features is not as widespread as the biological and chemical properties. Also, the effect of hydrophobicity on these properties is less than the biological and chemical features. However, the hydrophobicity phenomenon can improve these features. The impact of superhydrophobicity on other physical features has not yet been fully investigated and needs further research in this field at the future.

5.3.1.3.1 Anti-Reflection

The superhydrophobic anti-reflective coatings have been obtained via various chemical treatment such as replication process of polydimethylsiloxane treated by heptadecafluoro-1,1,2,2-tetra-hydrodecyl-trichlorosilane [65], SiO_2 treated by hexamethyldisilazane [69], polydimethylsiloxane nanocone cluster microstructures with different aspect ratios from anodized aluminum oxide template [107]. Also, using tetraethyl orthosilicate and hexamethyldisilazane as superhydrophobic sol and antireflective layer through (3-Glycidyloxypropyl)trimethoxysilane and octadecylamine led to prepare superhydrophobic anti-reflective coating [29].

5.3.1.3.2 Anti-Wear

It has been needed inorganic and metallic substances with hard nature to prepare the anti-wear feature. The common superhydrophobic substances such as organofluorine and organosilicon which based on organic compounds have not significant abrasion resistance. Therefore, the anti-wear superhydrophobic surfaces have been prepared using inorganic or metallic surfaces which have good abrasion resistance through superhydrophobicity. The polyhedral oligomeric silsesquioxane grafted by graphene oxide [71] as inorganic substance and also copper coated by CuZn_5 and AuZn_3 [78] as metallic to prepare anti-wear superhydrophobic surfaces were investigated.

5.3.2 Self-Cleaning

Typically, separating different types of contamination from the surfaces require considerable time and energy. Therefore, self-cleaning coatings

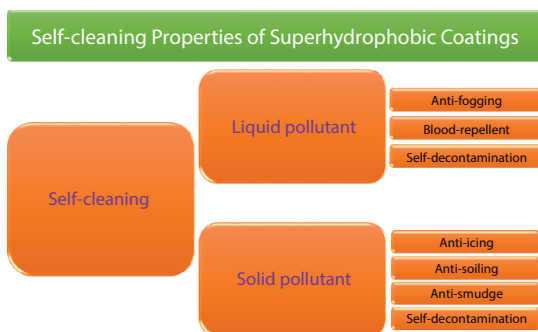


Figure 5.7 Superhydrophobic coatings application to clean up surfaces in different situations.

that were capable of spontaneously pollutant decontamination from the surface were rapidly expanded. The hydrophobicity attribute is one of the most important self-cleaning mechanisms in the coatings. The superhydrophobicity phenomenon which oriented from very low surface tension prevents contaminants adhesion on the surface. According to their physical form, the pollutants were divided into solid and liquid forms which showed in Figure 5.7. Typically, solid contaminants adhere to surfaces through physical interactions and static electricity while the adhesion forces of liquid contaminants are polar interactions in most cases.

5.3.2.1 *Liquid Pollutants*

The liquid phase pollutants typically have significant surface adhesion that lead to adhere to different surfaces. Liquid pollutants include polar and nonpolar compounds. The chemical structure influences on the type of interaction between the pollutant and the surface. Water is the most widespread liquid phase compound in the environment and also polar interactions are stronger than nonpolar interactions. It can be concluded that the self-cleaning feature via superhydrophobicity have significant importance. There are several researches about sticking liquid phase pollutants that have been done which are discussed in this section.

5.3.2.1.1 *Anti-Fogging*

The temperature reduction causes water vapor condensation and then formed water thin layer on the surfaces. Also, further lowering of

temperature leads to ice formation on the surface. The fog has been formed easily on different surfaces especially metals and glass. It could originate from considerable surface adhesion of water and polar structure of these substances. Therefore, superhydrophobic attribute can prevent fog formation on surfaces. The anti-fogging superhydrophobic properties on the aluminium surface was obtained via chemical etching and surface treatment with lauric acid [9, 53].

5.3.2.1.2 Blood-Repellent

The blood cleansing from the surfaces has considerable importance because the blood has high adhesion tendency which originates from polar bonds in blood chemical structure. Also, the blood remaining on the different surfaces leads to infection spread and transmission of pathogens. Therefore, it is important to prepare coatings or surfaces that blood does not stick to them. The blood repellency feature has been obtained through different chemical and physical treatment methods including silica nanoparticles modification by chlorotrimethylsilane [70], titania nanoflower surfaces via hydrothermal synthesis in presence of HF [108], roll-to-roll (R2R) manufacturing by shrinking a prestressed thermoplastic with a thin layer of silver and calcium [28], and laser ablation of titanium [109].

5.3.2.1.3 Self-Decontamination

Various types of liquid phase materials lead to contamination of different surfaces. The most important liquid phase pollutants are water-based mixtures and various solvents. The liquid compounds can cause surface contamination either in pure form and mixture with other substances. The liquid pollutants not only cause dirt and surface contamination but can also cause other destructive phenomena such as corrosion on the surfaces. Prevention of liquid substances remaining on the surface can prevent the occurrence of negative phenomena on the surfaces.

5.3.2.2 Solid Pollutants

The solid phase pollutants especially airborne particles cause significant pollution at various surfaces particularly in public places. Solid contaminants can be attached on the surface by static electricity, van der Waals, and hydrogen interaction. Therefore, extensive research has been done on this subject.

5.3.2.2.1 Anti-Icing

Ice formation on the surfaces in glacial conditions could lead to various types of problems on the surfaces such as corrosion and reduced surface performance. Therefore, preventing ice formation on the surfaces in glacial conditions is very important. There are various chemical [75] and physical [18] methods to create these types of coatings. Unlike the anti-soiling attribute which typically associated with physical interactions, the coatings anti-icing attribute is related to the ability of surfaces to prevent the ice formation. The ice formation prevention is originated from the prevention of hydrogen bonds between ice and surface. The superhydrophobic surfaces could have produce anti-icing feature through different methods such as the treatment of silica nanoparticles by 1H,1H,2H,2H-perfluorodecyltriethoxysilane [75] and polyzwitterion brushes [62] as chemical treatment, and also laser treatment of stainless steel surface [18] and plasma etching [85] as physical treatment.

5.3.2.2.2 Anti-Soiling

Dust particles on the surface are solid contaminant samples which can easily remove by the help of water-repellent coatings because water carries dust particles with it [10]. Also, the combination of anti-dust and anti-reflective properties will significantly reduce the absorption of dust and airborne particles on the surface [76]. The superhydrophobic surfaces with anti-soiling feature have been produced through chemical treatment functionalization of SiO₂ nanoparticles by different organofluorine substances including heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane [76], Tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane [110], and fluorinated acrylic emulsion [10] have been obtained.

5.3.2.2.3 Anti-Smudge

The superhydrophobic coatings can prevent adhering soot and other airborne particles to the surface. It have considerable important to keep surfaces clean against airborne particles and vehicle smoke pollution especially in crowded public places [111, 112]. The surfaces which have superhydrophobic and anti-smudge properties were obtained through chemical treatment by hydroxyl terminated polydimethylsiloxane and mono-di-hydroxy-terminated polydimethylsiloxane which are safer than fluorinated compounds [111, 112]. Also, surface treatment of SiO₂ nanoparticles by poly diallyldimethylammonium chloride and

fluorosurfactant layer leads to produce superhydrophobic anti-smudge surfaces [113, 114].

5.3.2.2.4 Self-Decontamination

Various types of solid pollutants can be placed on the surfaces which ice and airborne dust are the most common solid pollutants. Also, other contaminants can absorb onto the surface and contaminate the surface. It is also possible to absorb and transport other hazardous substances such as microbial and chemical contaminants through solid contaminants. Harmful and hazardous substances can be absorbed onto the surface of airborne solid pollutants and transported by wind. Therefore, it is important to remove solid contaminants from the surfaces. The repellent attribute of the superhydrophobic coatings causes easily separate different types of solid contamination. Other important aspect is the prevention of sticking moss [104, 105], fungi [17], chemical deposits [20], and other substances on the surface.

5.3.3 Smart Attributes

The preparation of polymers or coatings that can response to the external stimulant or, in other words, stimuli responsive has expanded significantly in recent years. In addition to the superhydrophobic attribute, these coatings also have an important ability to enhance their performance.

5.3.3.1 Conductivity

The most of polymer coatings and surfaces are electrically insulated. Therefore, conductive coating preparation had significant advantages. It is possible to prepare superhydrophobic and conductive properties simultaneously through chemical modification. This issue has been investigated in various recent studies. One-step vapor-phase polymerization of poly(3,4-ethylenedioxythiophene) in the presence of fluorinated decyl polyhedral oligomeric silsesquioxane and fluorinated alkyl silane [115], polypropylene treatment by vapor-grown carbon fiber and ketjenblack [116], textile coated by silver nanowire as conductive part, and also using carbon nanotube, polytetrafluoroethylene nanoparticles and fluoroacrylic polymer superhydrophobic part [35], polyurethane binding multi-walled carbon nanotube [117], superhydrophobic conductive sponge via WS_2 -Ag nanoparticles modified by polydimethylsiloxane [66] and glass treated by

silicone nanofilaments and carbon nanofibers [81] are some of researches which examine about superhydrophobic conductive coatings.

5.3.3.2 *Energy Storage*

The global warming, environmental and air pollution, fossil fuel reserves reduction, and the ozone layer depletion led to increased attention to renewable energies. The superhydrophobic coatings have important role to spreading renewable energies and energy storage. There has been extensive research on this topic in recent years which expected that the amount of research will expand significantly in the coming years. The superhydrophobic coatings cause to remain clean different surfaces against various contaminants. Therefore, it prevents the efficiency reduction of renewable energies generation or storage devices. However, this field requires much more researches. Beeswax coated by perfluorinated acrylic copolymer [61] disposable cotton balls treatment by surface-coating of Fe_3O_4 particles and post hydrophobic-modified treatment with long-chain silanes [60] and also microencapsulation of n-docosane with nanostructured ZnO/SiO_2 shell [77] are the examples of researches about this modern issue.

5.3.3.3 *Photocatalytic*

The simultaneous formation of superhydrophobic and photocatalytic properties due to increase surface responsiveness to environmental events. Hence, in addition to the contact angle, the presence of ultra violet ray can influence in the surface self-cleaning properties. This new issue has been found in recent researches such as one-step reaction of octadecyl isocyanate with TiO_2 nanoparticles [55], Ag_2O particles [79], and also glass beads modification by TiO_2 nanoparticles and silicone nanofilaments [27].

5.3.3.4 *Self-Assembly*

The self-assembly process is internal organization of mixtures which proceed in certain orientation without external directions. The self-assembled substances have special characteristics because of their special morphology. The self-assembled superhydrophobic coatings have special properties which examined in different researches that include pillar array formation in silk nanowires [118], triblock copolymer based on poly(dimethylsiloxane)-poly(tert-butyl acrylate)-poly(methacrylolsobutyl POSS) [73], and the pig fat coated by biopolymer and Fe_3O_4 [119].

5.3.3.5 *Self-Healing*

Self-healing as a superior feature in coatings leads to make coatings more durable. The mechanical stresses can damage the surface of superhydrophobic coatings. Therefore, the simultaneous development of superhydrophobicity and self-healing properties can increase the efficiency and durability of coatings. The surface treatment by hydrolyzed fluoroalkyl silane and fluorinated-decyl polyhedral oligomeric silsesquioxane [120], one-step vapor-phase polymerization of poly(3,4-ethylenedioxythiophene) in the presence of fluorinated decyl polyhedral oligomeric silsesquioxane and fluorinated alkyl silane [115], polydimethylsiloxane with flat lotus leaf [98], wood coated by polydimethylsiloxane as the base coat and waterborne perfluoroalkyl methacrylic copolymer- TiO_2 as the top coat [44], fabrics coated by polydopamine and stearic acid emulsion [54], cement modified by 1H,1H,1H,2H-perfluorodecyl trimethoxysilane [63], and also biomimetic polydimethylsiloxane via replication of shark skin and surface-initiated atom transfer radical polymerization 2-perfluorooctylethyl methacrylate [64].

5.3.3.6 *Stimuli-Responsive*

The ability of the polymers to respond to external stimuli is recognized as an advanced and novel feature. These smart polymers are capable to external stimuli responding. Therefore, research on these polymers is expanding at astonishing rate [121, 122]. Also, smart superhydrophobic coatings have been expanded in recent years. Some of the most important of these studies include poly-3-methylthiophene-carbon membranes as electro-responsive carbon membranes with reversible superhydrophobicity/superhydrophilicity switch for efficient oil/water separation [123], magnet-responsive fabrics treated by hexadecyltrimethoxysilane, polydopamine, and Fe_3O_4 nanoparticles [72], magnetically-responsive using polydimethylsiloxane and iron particles [67], and also fire-retarding magnetic-responsive superhydrophobic sponges through polydopamine treated by Fe_3O_4 nanoparticles and n-octadecyl mercaptan.

5.3.3.7 *Multifunctional Superhydrophobic Coatings*

The coatings which have at least three substantial and effective properties are called multifunctional coatings. Multiple appropriate properties of the multifunctional coatings lead to increase their applications [124]. The superhydrophobic multifactorial coatings can be prepared via chemical and physical modification methods. However, chemical modification methods

have more variety and versatility. The multifunctional superhydrophobic coatings which have been prepared via chemical treatment such as one-step vapor-phase polymerization of poly(3,4-ethylenedioxythiophene) in the presence of fluorinated decyl polyhedral oligomeric silsesquioxane and fluorinated alkyl silane [115], silica treatment by polymethylhydrosiloxane [125], polydimethylsiloxane with flat lotus leaf [98], copper coated by CuZn_5 and AuZn_3 [78], polyhedral oligomeric silsesquioxane-graphene oxide [71], TiO_2 treatment by octadecyl isocyanate [55], rubber treated by polydopamine and Ag nanoparticles [100], zinc sheet modified by NH_4F [99], cement modified by 1H,1H,1H,2H-perfluorodecyl trimethoxysilane [63], glass treated by silicone nanofilaments and carbon nanofibers [81], and SiO_2 nanoparticles treated by fluorinated acrylic resin emulsion [10].

Also, the superhydrophobic multifactorial coatings have been obtained through physical methods such as nylon mesh cover peeling from the surface of the concrete [103] and laser-induced graphene [83].

5.4 Conclusions and Summary

Useful properties of superhydrophobic coatings lead to increase attention and research about this issue. Non-stick surfaces cause to increase health and significant reduction in cleaning and protection costs. Various methods of chemical and physical modification to prepare superhydrophobic surfaces have been investigated. The superhydrophobic coatings not only lead to self-cleaning feature but also have some other valuable features. The superhydrophobic coatings are classified through substrate type, coating type, and also the characteristics which expected of the coating. Nowadays, the most attentions are paid to prepare smart coatings as well as multifunctional coatings. It originates from the ability to respond to external stimuli as well as to the ability to function in different environmental conditions. Preparation of superhydrophobic surfaces or coatings that are simultaneously both responsive to external stimuli and multifunctional have extraordinary importance. This significant challenge is being widely pursued by scientists that appropriate progress has been made in recent years.

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Adsorptive Polymer Coatings

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Abstract

Coating is referred as a covering of an object or substrate surface completely or partially which changes the properties of the substrate completely. Polymer coating is degraded when exposed to UV lights and thus failed to protect the layer. Therefore, to control the degradation of polymers, a new approach of adsorptive polymer coating has been employed. This chapter provides the brief view of adsorptive polymer coating and their coating techniques. This chapter also includes the comprehensive comparisons of coating techniques. Moreover, adsorptive polymer coating applications in various fields are also detailed. Furthermore, future perspective towards existing challenges provides a better direction and understanding to overcome these challenges in coming days.

Keywords: Coatings, adsorptive coating, coating techniques, coating applications

6.1 Introduction

The covering of an object usually a substrate is termed as coating which is spread over the substrate's surface. The applied coating may cover all over the surface completely or partially cover the substrate surface [1]. The morphological properties of an object, e.g., wear resistance, adhesion, wettability, and corrosion resistance, may be improved by applying coating. In

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some cases, coating adds new properties to the materials such as electrical conductivity, magnetic response, and the formation of an essential part of the finished products [2].

In the past decades, its use has become ubiquitous for protective, functional, and decorative applications [3]. The protective and functional properties include anticorrosive, ice repelling or oleophobic, hydrophobic, flame retardancy, antifouling, self-healing, self-cleaning, and antibacterial, etc. [4]. Thus, to control the corrosion/degradation rate of materials, the modification is the basic approach to employ noble coatings as physical barrier.

6.2 Types of Coatings

In order to protect the materials from degradation/corrosion and get the desired properties, various types of coatings are applied. Some of common types of coatings are illustrated in Figure 6.1.

6.3 Polymer Coating

All coatings, when exposed to UV radiation, start degrading due to complex photochemical process. This degradation is enhanced by the weather conditions such as temperature, pollutants, and moisture, etc.; however, polymer coating do not degrade as they do not absorb UV radiation greater than 295 nm wavelength [5]. Thus, polymer has been extensively been employed as coating material in various fields. Polymer coating enhances mechanical

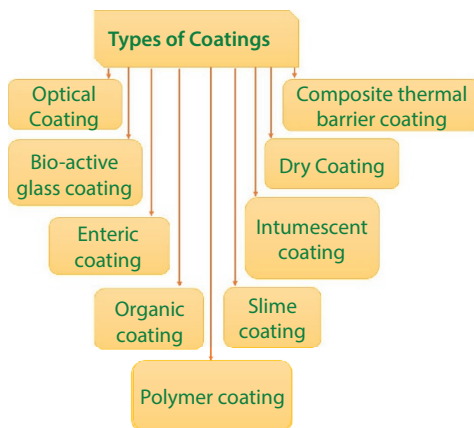


Figure 6.1 Various types of coatings.

strength, thermal stability, biomedical properties, separation characteristics, chemical resistance, and other various functional properties [6].

Polymer coating has various applications in the field of painting, storage media, semi-conductors, optical devices, fluorescent devices, and etc. [7]. Protection of material from closure stresses of the concealed materialization is a significant improvement of polymer coating. Polymer coatings also perform the protection of material from ambient conditions, abridged fragmentation, and protect from dusting [8].

6.4 Types of Polymer Coating

The concept of polymer coating suggests new routes in the vicinity of secure and durable materials and sustainability and improves the efficiency [9]. Polymer coatings are divided into different types as shown in Figure 6.2 depending on the superior properties in terms of stiffness, strength, thermal stability, cost, and light weight [10].

6.5 Adsorptive Polymer Coating

Adsorptive polymer has been proposed as an alternative coating materials in pharmaceutical, cosmetics, environmental, personal care products, food safety, and etc. [11–15]. Adsorptive polymer proposed large surface/volume ratio and present unique surface chemistry features, excellent porosity, good mechanical strength, and hydrophobic surface area. Increased consumer concern to food safety led to the development of adsorptive polymer coating, a renewable coating suitable for food, and pharmaceutical, etc. In food packaging, adsorptive polymer

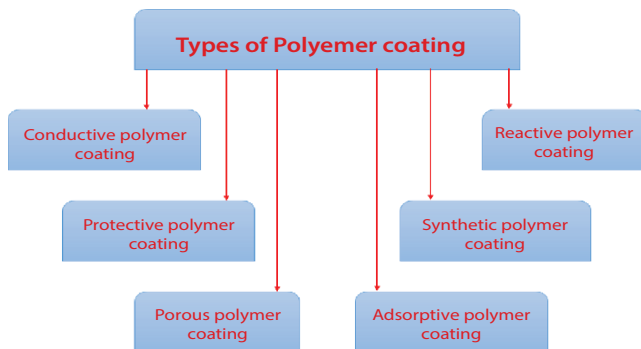


Figure 6.2 Types of polymer coating.

film perpetuate and insulate food from extrinsic chemical, physical, and microbiological elements [16, 17].

6.6 Materials

Numerous polymers have been used as coating material (shown in Figure 6.3). Polyethylene, polypropylene, polyethylene terephthalate, and nylon, etc., are common adsorptive polymers being widely used as coating material [18, 19]. Selection of polymers for coating depends on low price, low wettability, and excellent mechanical properties [20].

6.7 Adsorptive Polymer Coating Techniques

In adsorptive polymer coating, a polymer solution is filled in capillary that adsorb to the capillary surface that formed a dynamic coating or adsorbent is mixed with polymer. Various adsorptive coating methods have been established for coatings with thickness range of few nm to 10 nm, and numerous synthetic, natural, neutral, and charged polymers have been used in the pursuit of dynamic coating [21]. Some suitable coating techniques are shown in Figure 6.4.

6.7.1 Spray Coating

Spray coating is a facile and unique approach for applying a coat over a substrate. In this process, first suitable adsorbent is dissolved in polymer

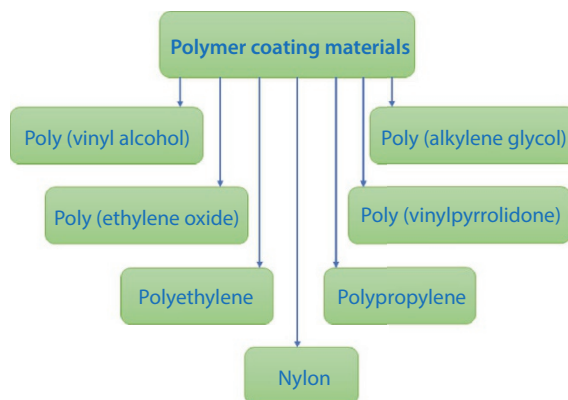


Figure 6.3 Common materials for adsorptive polymer coating.

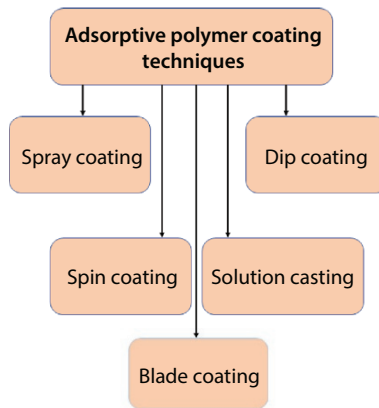


Figure 6.4 Adsorptive polymer coating techniques.

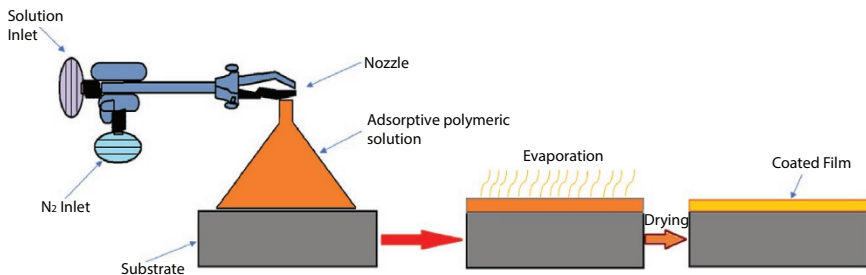


Figure 6.5 Spray coating technique on substrate.

and then dissolved or melted polymer is sprayed onto a substrate as shown in Figure 6.5 [22]. To generate continuous flow of droplets, the nozzle at the spray head atomized the desired material. For atomization process, the crucial process parameters such as surface tension, viscosity, nozzle design, and gas flow should be acknowledged [23].

6.7.2 Dip Coating

Dip coating technique is used to coat the three-dimensional object. In this technique, a solid object or substrate is submerged in polymer solution containing dissolved adsorbent as shown in Figure 6.6. The submerged object is withdrawn, solvent is evaporated, and object is dried at required temperature [24]. The important advantage of this technique is to obtain

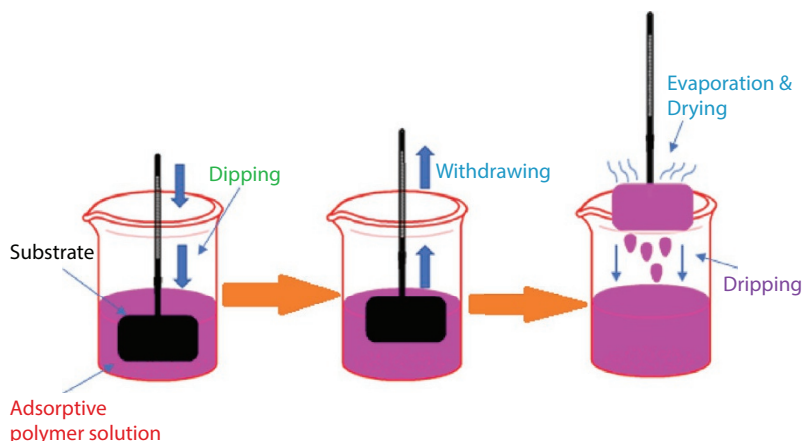


Figure 6.6 Dip coating technique on solid object.

uniform and high quality films. The controlling parameters such as submersion time, dipping cycle, withdrawal speed, solution composition, and concentration adjustment should be carefully acknowledged to obtain unique dip film thickness and required properties [25].

6.7.3 Spin Coating

To obtain high quality and fine films, spin coating technique has been employed. In this technique, centrifugal force spreads the coating material. A cramped quantity of adsorptive polymer film is pragmatic on the middle of the substrate as shown in Figure 6.7 [26]. Under centrifugal action, as the substrate gain required spinning speed, the coating material is spread

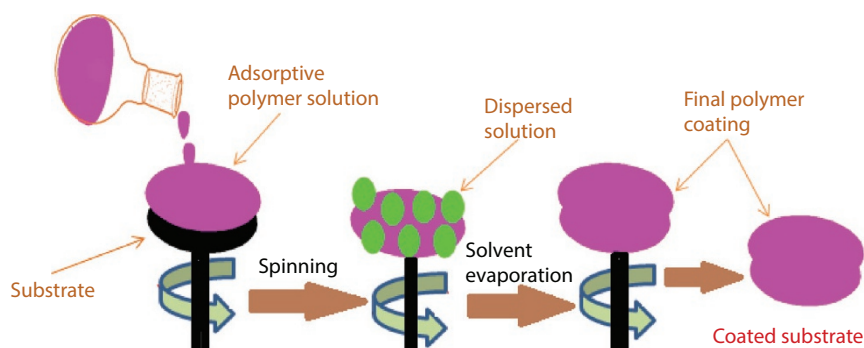


Figure 6.7 Spin coating on substrate.

on substrate. This is the most refined adsorptive polymer film forming technique, and covering instrument is named as spin coater [27].

6.7.4 Solution Casting

Solution casting is a simple coating approach. This method was developed to coat adsorptive polymer solution on a substrate. In this approach, the softened adsorbent in polymer solution is simply casted on the solid object and allowed to evaporate at desired temperature as shown in Figure 6.8. The obtained film on substrate or solid object acts as a coat and protect from external environment [28].

6.7.5 Blade Coating

To obtain thin film coating on substrate, blade coating technique is preferably used. In this technique, the dissolved selective adsorbent in polymer solution is layered on solid object with a high-pitched blade edge as shown in Figure 6.9. The volume of thaw or solution on surface of the material is controlled by the sharp knife edge [29]. Less volume of solution waste, consistency to a roll-to-roll fabrication, interlayer dissolution resistance, and large area uniformity are considered as the advantages of this technique and give well-defined coating. The fabrication parameters such as blade coating speed, blade gap, and solution concentration are properly adjusted to obtain optimized coating thickness [30–32].

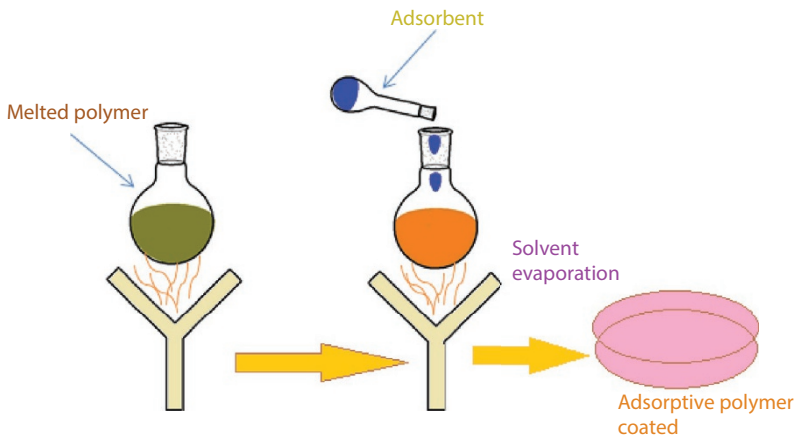


Figure 6.8 Solution casting technique.

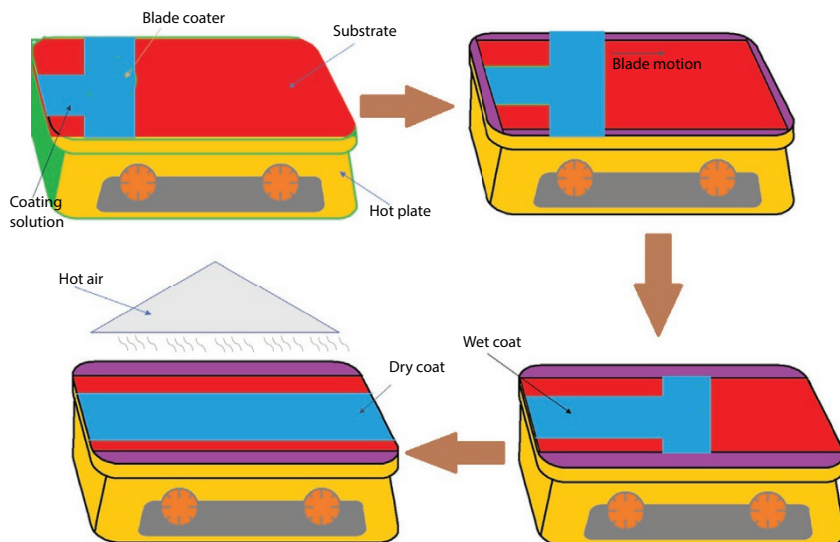


Figure 6.9 Blade coating technique on substrate.

In the absence of centrifugal action, polymer chains are free to move, which is an advantage of blade coating over spin coating. Therefore, there is no need of any kind of post treatment such as thermal and solvent annealing. Thermodynamically, more favorable morphology has been obtained through this technique due to slower evaporation of solvent [33].

6.8 Adsorptive Polymer Coating Applications

Adsorptive polymers are a viable candidate for coating of materials due to excellent thermal, chemical, and mechanical resistance and protect the material from deterioration. Due to these properties, a vast application of coating has been found in this regard. Some important and common applications are illustrated below.

6.8.1 UV Protection

When polymer coating is exposed to ultraviolet radiation, polymer degradation process accelerated due to breaking of polymer chains. The loss of surface gloss and significant deterioration of coating are resulted due to this degradation of chains as free radicals are produced which reduces the molecular weight of polymer [34]. However, adsorptive polymer material

has ability to adsorb photon in ultraviolet region which makes adsorptive polymer as an innovative candidate to develop the stabilization and weathering of polymer coating [35, 36].

6.8.2 Biomedical

Due to biocompatibility, elasticity, corrosion protection, and mechanical strength, adsorptive polymer coating is considered as one of the promise candidate for variety of biomedical applications [37]. In drug delivery application, this type of coating is considered very effective [38].

6.8.3 Corrosion Protection

Due to contact of metals with environment, devastation/deterioration of metals occurs. Thus, to prevent the materials from deterioration, different approaches have been developed so far. However, adsorptive polymers have excellent corrosion inhibit properties [39, 40].

6.8.4 Mechanical and Wear Properties

Adsorptive polymers managed to enhance the impact, flexural, and tensile strength because of the excellent adsorbent interaction and act as an intelligent stress transfer through the interface [41]. Adsorptive polymer coating also protects materials from galling, physical damages and seizing. This type of coating improves the toughness wear resistance of polymer coating. Thus, adsorptive polymer coating stemmed in a outstanding development in wear and corrosion resistance [42].

6.8.5 Packaging

Packaging of materials is a very common and important application of adsorptive polymer coating. Anti-microbial packaging materials have been investigated to hinder microbial growth in food [43]. To design and control food packaging process, release kinetics, diffusion mechanism, polymer kinetics, etc., are the essential parameter to be considered. For liquid food packaging, adsorptive polymer coating was also being employed [44, 45].

6.9 Future Perspectives

In each of above mentioned technological areas, several challenges for adsorptive polymer coating still exist. Intelligent inhibiting adsorbent are

also needed for ideal corrosion protection [46]. To obtain the better results and to control the coated film thickness, properties, morphology, and to obtain high performance for commercialization, a better understanding and relevant parameters optimization of processes needed [47].

Proper mixing of adsorbents in polymer and random aggregation of adsorbent is still a problem. Thus, this is indispensable to recognize the *in vitro* and *in vivo* approach for equalization of these coverings [48]. On large-scale application, quantitative analysis of uniformity is still lacking. Nevertheless, imminent exploration may undertake the complexities of these challenges and assist to gain excellent performance of materials and coatings [49].

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Polyurethane Coatings

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Abstract

Polyurethane belongs to a versatile category of polymers which includes a wide range of applications. It provides an excellent coverage to substrate for protecting it from wear and tear, abrasion, corrosion, and weathering. The complex chemistry of polyurethane has made its significant position among various polymers to dominate this important market. The significance lies in its leading role to replace conventional polymers by its unique formulations and development of both homogenous and heterogeneous emulsions. It provides a custom solution to décor and protect the surfaces and to probe the solution of the problems faced by polymer industry and allied industries. With the exception of few surfaces, PU is an eco-friendly dispersant to majority of surfaces which make it an excellent choice to be used with ease. Fast drying and easy curing without additional curing agents and variety of application methods enchant the consumer to use it on a range of surface.

Keywords: Polyurethane, formulation, coatings, protection

7.1 Introduction

The term “polyurethane” is employed for the polymers comprising a significant figure of urethane (ethyl carbamate) groups. In reaction between the hydroxyl group of the macrodiol/polyol and the isocyanate group, urethane linkage is formed, which is represented in Figure 7.1.

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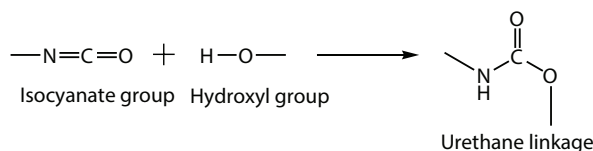


Figure 7.1 Representation of urethane linkage.

Like a conventional polymer, the name is derived due to repeated urethane linkages. Although, the usage of the common term polyurethane is illusive as polyurethane polymers neither belong to the class of polymers which consist of primarily urethane linkages nor they are synthesized by the monomeric polymerization of reactant urethane. The molecular chain in the major linkage groups is biurets, ethers, allophanate, and amides. The term is more frequently used for the expediency than accuracy [1]. The polymeric material of polyurethane has exclusive range of chemical and physical properties. Polyurethanes have gained attention in different industries, for example in adhesives, in the form of foams, as a thermoplastic elastomer and in coatings field [2]. Polyurethane has always been an emerging field of polymers and has enchanted the investigators to explore more and more about this material. It is an interesting system and its properties can be modified by the structural and chemical variation. Its broad spectrum ranges from soft flexible material to tough and rigid materials. It is hard like fiber glass, squishy like foam, protective like varnishes, bouncy like rubber, and sticky like glue.

These are widely distributed in the chemical, automobile, medicinal, packaging, computer, and athletics industries due to the fact that a large variety of raw material with the specific properties is available for polyurethane. In order to find out the best advantages of polyurethane polymeric material, the prime consideration is the enhancement of the steps of the process of synthesis [3].

Since its discovery, the polyurethane has been studied a lot by the researchers. They have developed the methods of its synthesis using linear and graft copolymers [4]. There are two convenient methods for the synthesis of polyurethanes, one shot method and the prepolymer method. Prepolymer method is considered efficient over one shot method due to its minimum chances of side reactions. Researchers have preferred prepolymer method over one shot method depending upon the requirement of the final product [5]. Polyurethane in various forms has been synthesized starting from rubber, elastomers, and foams, etc. They have been studied as thermoplastic elastomeric poly (propylene) system consisting

of a lined structure contained numerous blocks of stereo regular or stereo irregular arrangements [6]. Kim and Lee have prepared the thermoplastic PUs by different hard part length as of a fixed molar ratio of polyols and diisocyanate. They have adopted different polymerization procedures and have studied the consequence of polymerization technique on mechanical and thermal properties of polyether-based thermoplastic polyurethanes [7]. Detailed reviews on the material have also been reported extensively. Wicks and coworkers have reviewed the polyurethane system involving water as a carrier medium. They have described that the chemistry and the raw components usage in this ground and has offered some factors that should give attention in order to make this field feasible for the industry [8]. Chattopadhyay and Webster have presented a detailed review on the thermal stability and flame retardancy of polyurethanes [9]. Most useful, common, and research materials are polyurethanes in the world. Polymeric materials have special groups like polyurethanes. In between the large number of plastic types, polyurethanes are different in numerous ways. Polyurethanes can be combined with variety of materials such as integral skin, paints, elastic fibers, liquid coatings, foams, insulator, and elastomers. During World War II in place of rubber, polyurethanes were first developed. Polyurethanes can be incorporated in different applications because of its versatility and appropriateness [10]. Polyurethanes have many superior properties like hardness, strength, modulus, and elongation. Because of these properties, polyurethanes are broadly used in various applications like building and construction applications, textiles, in biomedical, in automotive industry, etc. In polyurethanes, most repeating unit is urethane group. Along with urethane group, there are many other groups present in polyurethanes, for example, urea, ether, ester, or aromatic compounds. Synthesis of polyurethanes can be done by a wide range of sources and because this polyurethane gives a large no of specific applications. On the basis of required properties, polyurethanes can be classified into various groups like coating, elastomers, rigid, waterborne, flexible thermoplastic, adhesive, and sealants. Among the main applications of polyurethanes, very prominent polyurethane product is polyurethane foam. This product is used globally. There are several types of polyurethanes foams. All these types are of commercially significant. These are divided into these major types, for example, adhesives, rigid foams, surface coatings, elastomers, integral foams, and flexible foams [11]. Thermoplastic polyurethane as for its good strength, excellent abrasion resistive, brilliant chemical resistive, and have low smoke properties. This polymeric material is extensively used in the form of sheathing composite in particular determination, low voltage control cables, and also in the profile extrusions. It is proven that

polyurethanes have fascinating shape-memory qualities. Shape-memory PU_s is abbreviated "S-PU_s." Shape memory polyurethanes are consist of polyester and polyether, molecular weight of 300–1,000. Shape memory polyurethanes are set in a definite shape above Glass transition temperature and cooled to a temperature below glass transition temperature. Shape memory cooled polyurethanes hold this particular shape as it is set. By heating shape memory polyurethanes to a temperature above glass transition temperature, the shape memory polyurethanes came back to their original shape.

Rigid polyurethane foams (RPFs) are three-dimensional polymeric substances, cross-linked, and possess cellular structures. Rigid polyurethane foams have low thermal conductivity or excellent mechanical resistance. Rigid polyurethane foams are used by means of insulating materials, refrigerator (domestic/commercial), in the field of building engineering, in automotive parts, and use in pipelines applications [12].

7.2 Chemistry of Polyurethane

Compounds which consist of hydroxyl groups mostly produce esters of substituted carbamic acid and urethanes. These consistently procedure portion of the end usage on the way to which the isocyanates are placed. The term polyurethane has turn out to be accepted by means of a generic term in order to cover the entire engineering products produced from isocyanates [13].

Polyurethanes are produced in presence of ultraviolet light activation, catalyst, chain extender, or any additives, by means of a chemical reaction among a di/poly isocyanate in addition of a diol or polyol, creating repeating urethane groups. In polyurethane backbone, urea, ester, aromatic ring and ether are present with urethane linkages [14]. The polyurethanes chemistry allows this class of polymers to assemble with further compounds that are mostly cooperatively termed to as reaction polymers. Such mixtures consist of epoxies, unsaturated polyesters, and phenolics [10].

Isocyanates stay reactive class, at room temperature isocyanate reacts by hydroxyl comparatively slowly. To some degree, the slow speed of isocyanate reaction is a reflection of phase unsuitability of the comparatively nonpolar or thicker isocyanate phase and comparatively polar or less-dense polyol phase. The reaction also remains slow at room temperature even if phase compatibilized with a surfactant [15]. Polyol molecules must certainly consist of two or more than two isocyanate groups ($R-(N)C]O)n\$2$)

and hydroxyl groups ($R_0-(OH)_n$), correspondingly. The shown qualities of the polyurethanes frequently rest on the categories of polyols and isocyanates by which they were prepared. Usually, soft flexible polymers can be obtained by the means of flexible long segments of polyols, although rigid or hard polymers can be prepared by a greater cross-linking amount. Stretchy polymeric substances might produce via elongated chains through low cross-linking, while hard polymers can be generated by the help of shorter chains within high cross-linking. A mixture of long chains by means of normal cross-linking, generate such polymeric material which are appropriate aimed at foam manufacturing. In polyurethanes, because of the presence of cross-linking, they frequently own an immeasurable molecular weight by means of a three-dimensional (3D) network build-up. Because of this motive, a small portion of polyurethanes can be mentioned to as a giant molecule.

This could also describe why typical polyurethanes frequently will not undergo melt and soft after they are heated. The addition of various additives into the isocyanates or polyols, and amendments to the processing settings, makes it probable to acquire an extensive series of characteristic features, which able them to be used for numerous applications. Various forms of polyols are available. By the use of various methods, all these polyols can be produced in laboratories [1].

Under the existence of catalyst by polyaddition reaction in alcohols and isocyanates, synthesis of polyurethane is carried out (Figure 7.2) [16]. This polyaddition reaction is nucleophilic addition in nature, in which different catalysts are used, for example, compound like organotin, metals, and tertiary amines. Urethane formation is in fact an equilibrium reaction; the presence of a catalyst therefore also increases the rate of the reverse reaction at very high temperatures. Another important basic reaction involved in the polyurethane formation is the chain extension reaction which occurs between chain extender (diol or diamine) and isocyanate. The use of diol as chain extender generates urethane, while in final step of synthesis of polyurethane, diamine reaction produced urea linkages [17].

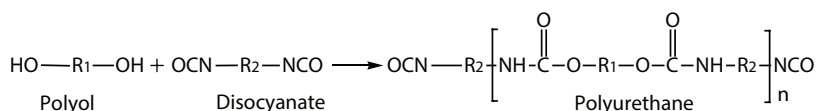


Figure 7.2 Reaction for the synthesis of polyurethane.

7.3 Formulation of PU Coating

7.3.1 Raw Material for Polyurethanes

7.3.1.1 Polyols

Polyols or macrodiols are reactive compounds which are usually found in the form of liquids, but are available in the solid form as well. These contain at least two functional groups in the form of hydroxyl or amino groups. A huge variety of polyols are accessible, but most of the polyols belong to two classes, hydroxyl terminated, and amine terminated polyols. So, depending upon the use of the starting polyol of polyether, polyester, or hydrocarbon materials, we can obtain ether-based, ester-based, or hydrocarbon-based polyurethanes as a finished product.

7.3.1.2 Polyether Polyols

This raw material has repeating linkage of R-O-R. They have two or more functional groups (hydroxyl groups) at the terminals. The reaction of epoxides like ethylene oxide or propylene oxide with the multifunctional initiator in the presence of a catalyst forms the polyether polyols. Common polyether diols are polyethylene glycol, polypropylene glycol, and poly (tetramethylene ether) glycol. Polyether polyols contribute about 90% to the industries. The hydroxyl groups of polyether can react with the other substances, e.g., isocyanates to develop urethane linkages. These are water soluble compounds and are available in a wide range of molecular weight 200 to 14,000 daltons. The physical properties of the material depend upon the chain length of the polymer. Their major contribution is in the polyurethane industry for the manufacturing of different products. These are mainly used in the form of polyethylene glycols or polypropylene glycols. Polypropylene glycol is similar to polyethylene glycol in most of its properties and is used in the same way as other polyether polyols (Figure 7.3).

Polyether polyols have always been used widely for the production of various polyurethanes. These polyethers have been used in the production

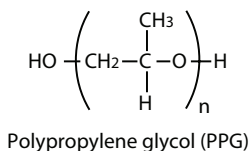


Figure 7.3 Chemical Structure of PPG.

of moisture curable and polyurethane resin, and these resins have been used as an adhesive on plastic and aluminum substrates [18]. While, polypropylene glycol with different molecular weights has been used for polyurethane plastic bandages [19].

Synthesis of polyurethane with cycloaliphatic diisocyanate has been carried out to study the structural investigation by the use of 1D and 2D NMR spectroscopy. In synthesis of polyurethanes, polyols are used. Polyols have mono disperse rigid segments [20]. Cross-linked polyurethane has also been formed in this connection. Blending of polyether and polyester polyols is also a common practice for the production of polyurethanes. Different synthesis protocols give different properties [21].

7.3.1.3 Hydrocarbon-Based Polyols

Hydroxyl-terminated polybutadiene HTPB is a commonly used hydroxyl compound in the polyurethane industry [22]. The complete hydrocarbon nature and unsaturation in the backbone make it a useful macrodiol for various polymeric products. Polybutadiene are very interesting compounds because of their very low T_g (-80°C) and lead to final materials with good viscoelastic properties [23]. HTPB produced strongest polyurethane. The low T_g and hydrocarbon-based backbone structure of polybutadiene impart better hydrolytic properties and higher flexibilities in the final product. However, the mechanical properties such as tensile strength, abrasion, and tear resistance are not considerably high for these materials [24]. Hydrocarbon-based polyurethanes develop phase segregation due to presence of a polar character of oligobutadiene. Consequently, some striking properties, for example, at low temperature retention of elastic behavior, highly resistive to acid or base hydrolysis, low water penetrability, and upgraded mechanical properties, have been established. Final product gain is much more beneficial properties in the presence of HTPB (Figure 7.4) [25].

The complete hydrocarbon nature of polybutadiene prevents formation of inter segment hydrogen bonding which are usually present in polyether or polyester-based polyurethanes favoring phase segregation [26].

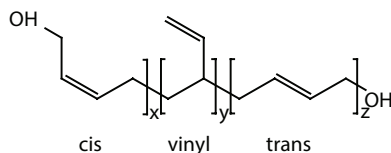


Figure 7.4 Chemical Structure of HTPB.

Polybutadiene in the form of a mixture with polystyrene blocks has been used to study the adhesive properties of the system in terms of peel and tack; the tackifiers have also been incorporated to check the effect as cross-linking agents [27]. The modification of the system has been used to improve the adhesive properties [28, 29]. The functionalization of HTPB is a common practice for the polyurethane formation and has been carried out to use in various properties as well [30]. Along with various properties of the material, the rheological properties have also been studied [31].

7.3.2 Isocyanates

The chemical structure of diisocyanate can be classified into two kinds. One is aromatic diisocyanate, and the other is aliphatic one. The PUs prepared with aliphatic diisocyanate does not show the change of color by UV light, heat, and aging [32]. With the help of resonance structure, high reactivity of the isocyanate group can be demonstrated (Figure 7.5). Lowest electron density is associated with carbon atoms, while higher electron density is at the oxygen atom. As an immediate consequence, the carbon atom has a positive charge, the oxygen atom has a negative one, and the nitrogen atom with an intermediate negative charge.

The free isocyanate contents influence the adhesive properties of the polyurethane [33]. The hydrophilic isocyanate has been reported to form stable and homogenous micelles in water [34]. The researchers have also found out that the self-curable polyurethane can be prepared by the use of aliphatic diisocyanate [35]. Polyurethane coatings were particularly used for impregnating paper and in the manufacturing of garments that remained resistive to mustard gas or rusting. For the purpose of coating of metals, high brightness textures used for airplanes and wood, polyurethanes coating behaves as chemically resistive. The initial industrial manufacturing of polyurethanes coatings started with various preparations for specific purposes. Initially, polyurethanes coatings were frequently used in adhesives, elastomers, rigid forms, and coatings. After that, relaxed and convenient pillows prepared by means of flexible foams which are commercially available. Furthermore, the development of elastic foams from inexpensive polyether polyols directed to various automotive or upholstery applications that are still applicable today. In coating, polyurethanes have a wide application,

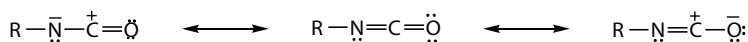


Figure 7.5 Resonance structure of isocyanate groups.

because of their specific qualities: low temperature flexibility, corrosion, toughness, good mechanical strength, excellent abrasion. Polyurethane elastomer is one of the significant kinds of polyurethane. In different engineered products, polyurethane elastomers are incorporated. Their processing is easy because of the fact that they are malleable. Recycling possibility of polyurethane elastomers is high [1]. Some additives used in the synthesis of polyurethane and their advantages are listed in Table 7.1.

Table 7.1 Advantages of PU components.

Components	Advantages
Fillers	Fillers are used to enhance the properties of the material, for example, tensile strength and stiffness.
Catalysts	Catalysts are used to accelerate the rate of reaction between polyols and isocyanate and because of this even at lower temperature reaction can be carried out.
Smoke retardants	The main use of smoke retardants is the reduction of the generation of smoke during the burning of materials.
polyols	The main advantage of polyols is the contribution of flexible long segments, in result of which soft elastic polymers are produced.
Plasticizers	In order to decrease the hardness of the materials, plasticizers are used.
Isocyanate	Isocyanates are used to enhance the properties of polyurethanes, for example polyurethane curing and reactivity.
Pigments	Pigments are used in the production of polyurethanes colored materials, particularly for the purpose of aesthetic properties.
Blowing agents/ surfactants	Blowing agents/surfactants are used in the synthesis of polyurethanes foams, also used to control bubbles formation and cell structure of the foam during synthesis.
Flame retardants	Flammability of the material is reduced by the use of flame retardants.
Cross-linkers/ chain extenders	Cross-linkers/chain extenders are used to enhance the properties of the material for example enhance mechanical support and modification of structure.

7.3.3 Monomeric Diisocyanate

In polyurethane products major value-added building blocks are monomeric diisocyanate. In coating industry, they are widely used. There are two types of monomeric diisocyanate aliphatic and aromatic diisocyanate monomers. Both monomers have important differences. Aliphatic diisocyanate is less reactive as compared to the aromatic diisocyanate. Urethane products prepared from aliphatic diisocyanates, if exposed to UV light, oxidize less while show more oxidation if prepared from aromatic diisocyanates. The furthestmost significant monomers used in the polyurethane engineering are toluene diisocyanate. In the:

1. Toluene diisocyanate is used in the form of raw material in the synthesis of adducts and prepolymers in coatings industry.
2. To gain extensive industrial uses, diphenylmethane 4,4'-diisocyanate was first diisocyanate monomers.
3. Hexamethylene diisocyanate is used for the synthesis of vast variety of polyisocyanate adducts. Hexamethylene diisocyanate is diisocyanate monomer used in exterior coating [36].

7.3.4 Vegetable Oil-Based Polyurethane Coating

From various diisocyanates, chain extenders, and polyols, polyurethanes have been produced and properties of polyurethanes are examined. By means of petroleum source, most of the polyols are generated and used in the synthesis of polyurethanes. But because of environmental concern and high energy strains of the process of preparation have emphasis on the requirement for further appropriate or environmentally friendly replacements. This draws more academic and commercial attention renewable resources, for example, vegetable oils [10]. Many researches are dedicated to the production of polyols from various vegetable oils, for example, palm oil, rapeseed oil and soybean oil [13]. Vegetable oils primarily contain triglyceride molecules with various reactive places, such as ester, hydroxyl groups, and carbon-carbon double bonds [10]. It is necessary to functionalized vegetable oils for the production of polyurethanes. This functionalization is done by the help of double bond reaction, for example, hydroformylation, epoxidation, metathesis, and ester bond reaction [13]. Polyols attained by the source of vegetable oils can be able to partially replace polyols derived from the petroleum source, particularly cross-linked by various kinds of isocyanates for the manufacturing of polyurethanes [10].

In the composition of polyurethane foam, the usage of polyols from vegetable oil source makes it conceivable to expand the qualities of some prepared foams, specifically hydrophobicity. Polyurethanes from vegetable oil polyols can be characterized to have higher thermal stability as compare to those synthesis from propylene oxide polyols [13].

7.3.5 Water Borne Polyurethane Coating

For high-performance coating systems, solvent borne polyurethane sets high standard. The demand of environmentally friendly substitute and high performance of coating gave a new solution to the coating formulator and waterborne polyurethanes have been offered. To fulfill the performance demand of many coating applications, many waterborne technologies has been offered. Currently, as compare to solvent-based products, waterborne products because of their low toxicity dominate coating industry gradually. In mark by this tendency, in last decades, aqueous polyurethanes have grownup commercially because of environmental concern [36].

Bayhydrol Polyurethane Dispersions

Polyurethane dispersion can be described as a colloidal system in which particles of polyurethane are spread in a continuous phase (water). The structure of a polyurethane dispersion resin type is shown [36].

7.4 Applications of Polyurethane Coating

Polyurethane coatings have vast applications in various fields and some of which are listed below.

7.4.1 Multifunctional Polyurethane Coating

Presently elastic fibrous textile functional materials have gained much attraction because of wide range of applications they posses like anti-bacterial, UV blocking, electrical conductivity, fire retardant superhydrophobic properties. There are many approaches to impart these functional properties to the fabrics, for example, submission of molecular layer-by-layer self-assembly, pad-dry cure, solgel method, UV curing, magnetron sputter technique, and plasma-induced graft polymerization techniques. Far-infrared rays having a lengthier wavelength of 6×10^5 mm can penetrate 2e3 mm hooked on utmost living ingredients and at molecular level they have strongest rotational or vibrational properties, because this dilation

of blood vessels takes place, or consequently enhancement of metabolism and blood microcirculation.

Far-infrared releasing ingredients absorbed energy from either heat of human body or from sun light. Far-infrared releasing ingredients can convert this energy into far-infrared rays having definite wavelength and, at that time, reemit these radiations in to humans. Far-infrared radioactivity gains much attention to claim of germanium or ceramics to textile materials, and these have nearby interaction with the human body, like cushions, sheet supplies, and clothing for health care and therapeutic determinations, because far-infrared radioactivity increases metabolism, enhance blood circulation, or encourages the regaining of exhausted muscles.

Researchers found that if we coat textiles with graphene graphene composites, we can gain a large number of important multifunctional properties, for example, thermal conductivity, anti-bacterial activity, and electrical conductivity. The graphene's potential is not investigated to enhance far-infrared emission. Consequently, as a functional unit to treat fabrics, graphene nanoplates applied. By doing this, far-infrared radiation and many other specific properties can be achieved by graphene [37].

7.4.2 Self-Cleaning of Polyurethane Coating

With passage of time, all surfaces are going to get fully contaminated in a natural environment. It consumes high efforts to clean these surfaces, surfactants used for cleaning also imparts negative impact on the environment. By the use of simple rain shower, dust from the leaves of many plants can be cleaned completely. The term superhydrophobic is used for these kinds of leaves. That is water dewdrops form spheres by very slight adhesion to the surface and then roll off very rapidly even at slight inclinations. On micro or nanometer scale, roughness is the main feature of superhydrophobic surfaces. Only on the tips of these structures, dirt and water droplets lie. Because of this, low adhesion forces are developed between the contaminating particles and rough surfaces. And consequently, by the help of rain shower, these contaminants can be washed out very effectively. In case of artificial superhydrophobic surfaces, self-cleaning qualities are not investigated yet. By means of chemical treatment, it is possible to hydrophobized silicon wafer specimen having different and even arrays of spikes. It can be used as a replicate of water repellent leaves. Likewise, hydrophobization of metal foils was carried out by the help of fluorinated agent. By the use of artificial fog, removal of contaminants is not possible because they have two levels of roughening. These surfaces can be cleaned perfectly

when water drops have kinetic impact energy. Self-cleaning property of coating materials is of great importance to avoid and elimination of pollutants. Because of the presence of C-F bond in the fluorocarbon, they possess low surface energy and have excellent self-cleaning properties. Because of this, the use of fluorocarbons as having self-cleaning property gains much attention [1–3]. In case of coatings that are fluorine modified, possess surface free energy and their efficiency as a self-cleanable agent to eliminate the pollution are not much satisfactory because of having great content of fluorine. This is not best way to measure cleanable property of any coating. Because of this reason, a test named peel test was introduced to measure the ability of cleanliness of coating material. In pressure sensitive coatings, peel test is used to measure the content of adhesion, when we detached coated film from substrate [9]. By elimination of adhesion from the pressure sensitive adhesive and surface of fluorine coating, peel test is used to measure cleanability. Because of extensive range of applications in different kind of fields like cements, glass windows, and in textile industries, this technology has been widely used. On contrary of these beneficial aspects, these coating have many additional benefits, for example, by using this approach, there comes reduction in the cost, uses in snow preservation, and give shield from ecological legislation. There are two types of self-cleaning coating: hydrophobic and hydrophilic coatings. These both categories clean themselves by the use of water. Hydrophilic coatings clean themselves by spreading water over the surface by setting themselves, in this approach, breakage down of pollutant particles is carried out. Hydrophobic coatings clean themselves by the rolling of water droplets on the surface, in this way, dirt is removed. All types of coating are also associated with some limitations [7].

7.4.3 Self-Healing of Polyurethane Coating

Great attention is given to the self-healing materials because they possess excellent potential to reduce the effect of degradation and also diminish the cost of maintenance. These kinds of polymers or composites have the ability to heal themselves in case of any damage where and when necessary. This self-healing behavior is stimulated by biological systems in which self-healing is usually a common routine. Materials like autonomic healing ingredients possess very good potential in industrial system because of the quality that they react deprived of external intervention to ecological stimuli in a nonlinear or productive fashion. Such self-healing coatings are of interest which can prevent and cure rusting of the underlying surface. In order to achieve the self-healing properties, many approaches are used,

some of which are reversible chemistry, polyionomers, encapsulation, hollow fibers, microvascular networks, monomer phase separation, and nanoparticle phase separation [38].

Majority of self-healing system have limitations like chemical and mechanical, which inhibit the use of these systems in coating. In case of self-healing systems, where environmental contamination can principally be avoided, it is necessary for a self-healing coating that it should be extremely stable to species existing in the environment. Because of air and water stability, self-healing chemistry is attractive.

And these self-healing systems remain stable even after exposure to high temperature. These properties enable the use of self-healing in thermal cure. Mechanical strength is of secondary importance in the field of coating system. Encapsulation of both of the phases (the healing agent and the catalyst) is beneficial in cases where the matrix can react with the healing agent [39].

Polyurethane polymer substance has a wide range of properties because of which this polymeric material used in the field of coating, such as they possess hardness or flexibility, they are good abrasion resistive, etc. Initially, this coating approach was formulated in presence of organic solvents but these synthesis protocols are substituted by the water-based approach throughout polymerization [1, 2]. One main drawback of water-based approach consists of polar groups, so there is a need of extra attention in order to stabilize water-based dispersions. Because of this factor, different properties reduce which inhibit the use of this dispersion in high application of high performance. However, by the use of cross-linking polymers, performance behavior of water-based dispersions can be increased [8, 9].

7.4.4 Nanodoped Polyurethane Coating

For the purpose of modification of physical characteristics, one of the best methods is material doping. For example, poor electrically conductive silicon (Si) can be doped with arsenic or boron in order to make perfect hole and electron conductor correspondingly. The more attention is on self-heating property of electrically conductive composites, grounded on polymers filled with graphitic nanofillers is presently increasing for various applications, for example, anti-fog devices, anti- and de-icing systems (ADIS), or self-curing process. Although, it is required to expand the information about the electrothermal performance of such kind of materials [40].

7.5 Advantages of Polyurethane Coating

Polyurethane coatings have a large number of advantages. Some of these are discussed below.

7.5.1 Biodegradation of Polyurethane Coating

Polyurethanes are vulnerable to degrade themselves, even after the years of synthesis. There are differences in the degradation behavior of various samples of polyurethanes that were attributed to the large number of properties of polyurethanes like topology or chemical composition. In case of synthetic polymers, there exhibit the regularity which allows the chain of polymer to pack easily. In result, crystalline region is formed. This limits the polymer chain accessibility to degradative agents. In polyurethanes, microbial degradation depends on various qualities of the polymer, properties like crystallinity, molecular orientation, cross-linking, and chemical groups existing in the molecular chains which govern the approachability to degrading-enzyme structures. In microbes, esterase activity has been noted. This activity allows them to the use of polyurethanes. Because the esterase enzymes are used in ester bonds hydrolysis, the microbial degradation of polyester polyurethane is theorized. In the medicinal field, polyurethanes display strong resistive property to macromolecular oxidation, hydrolysis, and calcination. Elastomers of polyurethane are actually cast-off in place of other elastomers because of their higher toughness, good elasticity, oxidation, excellent resistance to tear, and humidity [41].

7.5.2 Antimicrobial Activity of Polyurethane Coating

Antimicrobial coating is used to reduce the growth of injurious bacteria. Because of the hygiene issues in everyday's practical life and in the medicinal field, antimicrobial coating gains much attention. While on the exposure with the atmosphere, or when used as coating material, or used as an adhesive, polyurethanes are expected to microbial attack. Blistering and disbanding of coating takes places because of the micro-organisms attack under different kinds of sever conditions of the environment. In marine technology, one of the main issues is bio-fouling, being natural phenomenon. It also causes an issue in the marine navigation. When organisms are accumulated on the surface of the submerged vessel of the reaction, this results in the higher fuel consumption and because of this speed is also reduce. Organisms like algae, tubeworms, and barnacle accumulates on the surface of submerged vessel.

To overcome these issues, anti-fouling paints are used to give the protection of the submerged surfaces against the marine bio-fouling. Anti-fouling paints can be described as the paints consist of biocidal species. Organotin compounds are the most effective ingredients of anti-fouling paints. TBT (tributyltin compounds) and its derivatives were found to be destructive molecules to aquatic eco-systems. Because of this reason, TBT-based paints/compounds are entirely forbidden. Compounds contain of mainly heterocyclic ring in their structure, and their derivatives are used in the field of the medicine. Coumarin complexes and their derivatives constitute a cluster of additional forty drugs, which are extensively used in the medicine field as a hypertensive, anticoagulant, immunomodulant agents, antiarrhythmic, and they own extraordinary properties in contradiction of bacteria and fungi. In addition to this, the above stated compounds (coumarin) have different substitutions thiazol rings. This shows good biological activities. Because of these biological activities, coumarin group chemistry gains much attention of synthetic chemists. Such compounds which consist of thiazol rings in their structure also belongs to the heterocyclic compounds. Because of their potential chemo- therapeutic properties, these kinds of groups possess extensive range of biological activities and have good impact in the field of the medicine. In all kinds of available penicillin's, the main integral part is thiazol nucleus which helped in the development of the treatment of the bacterial diseases. In the treatment of the microbial infections, thiazols also have a great impact. In different chemical compounds, the parent material is thiazol, which includes biocides, dyes, sulfur drugs, chemical reaction accelerator, and fungicides. 2-aminothiazol-derivatives are described to display important biological activities and are extensively used as medicines. In addition to this, coumarin thiazol is found to be the best anti-microbial and anti-cancer agent. By saturating bactericidal materials with the help of some anti-bacterial agents, bactericidal material is prepared. The efficiency of such structures is founded on the slow release of the anti-bacterial agents in their surroundings with passage of time. Anti-bacterial agents like quaternary ammonium compounds, antibiotics, halogens, and silver ions. Consequently, this approach is proved to be very effective approach. Active biocides exhausted with passage of time. Along this, leaching of heavy metal ions and toxic biocides into the environment is not anticipated from an environmental point of view [41].

7.5.3 Cloth Protection

To protect the surroundings where we used to live and work becomes even more complex day by day. Traveling from one part of the Earth to

another part becomes easier even you can travel throughout the space. We belong to develop civilization where we can assess the incoming potential dangers around us, no matter where we are, all we need is anti-hazard environment.

Similarly, we also need protection in clothing industry. There is now an extensive range of cloth protection available, and continuous development of new raw materials helps to protect human beings from many hazards. Coatings are used in the form of laminations on the clothes in the pattern of continuous films to protect the well-being from the hazards of surrounding by the method of isolation. If we give treatment of water repellency to our fabric material, resistance to the wetting can be developed. Coating or protecting is broadly used in the protection of clothes, and to protect the films, in addition to this, the way or method by which these coatings are combined with the clothing assemblage, are of leading reputation to the manufacturing of a satisfactory clothing. Permethrin is an artificial made pyrethroid pesticide which associate to the compulsory properties of hot-feet, residual activity, repellency, and kill, and knockdown has extensively been used for periods of time, in cloth impregnation used as an arthropod interaction repellent. Consequently, permethrin is categorized by a higher level of potential in contradiction of a extensive variety of multiple repellent, vector insects or ticks, and toxicological effects on arthropods, rapid reactivity, excellent photostability resistance to weathering, and low mammalian toxicity. The combination of permethrin compound into human fabrics and exterior protecting devices essentially can be accomplished safely. Consequently, the use of permethrin is less expensive and easy to handle.

7.5.4 Anti-Scratch and Anti-Algal Coating

Presently, on the manmade exteriors such as roof tiles and buildings, the development of green algae is a main possible health and environmental problem. Because of this, it gains much attention. Because of the green algae, surface discoloration takes place which composed of corrosion and accelerated weathering. Additionally, anti-scratch and anti-algal coatings also have many other side effects, for example, diarrhea, asthma, respiratory failure, heart attack, liver cancer, itchy skin, fever, vomiting, seizures, paralysis, and DNA damage. If the toxins are consumed in large amount then results are even worse. It is necessary to control these green algae on the surface and it is also required to introduce such effective methods which are able to reduce the disadvantageous human health influences of these poisonous green algae.

Different core shell particles are synthesized; they cover the broader spectra of multiple applications. For example, silica-titania core-shell nanoparticle's utilization in nanopaint application by the use of anti-scratch quality of silica in the form of core material and anti-algal qualities of titania in the form of shell components in a single composite particle.

In coating industry, the use of Pus can increase the life span of the product and also increase product's appearance. Polyurethanes (Pus) are associated with the property of the strong bonding. Contrary, polyurethane sealants are associated with the property of providing tighter seals. Polyurethanes elastomers offer higher stress recovery and highly resistive to ecological conditions as these elastomers are much lighter than metals and can be into any desired shapes [42].

7.5.5 Flame Retardant Waterborne Polyurethane Coating

Polyurethanes have excellent chemical resistance, elastic properties, good hardness values, mechanical properties, and high abrasion. All these properties of polyurethanes increase its demand in the field of coating industry. Polyurethanes have strong impact to be used as fire hazards and ongoing public awareness about this impact forces the coating system to development of fire-retardant polyurethanes. By the addition of other reactive or non-reactive fire retardants, it is possible to enhance the flame resistance of a polyurethane coat. Addition of the reactive specie is preferable. As compare to the non-reactive class, reactive class of additives on the polymeric surface do not diffuse and, because of this reason, behave more effectively as resistive to combustion for a long period of time. On the lesser extent, they change the properties like (physical/mechanical) of the material in which they are incorporated. We can classify flame retardants as inorganic material or as an organic material. Inorganic materials include metal hydroxide, metN borates, and metal oxides. While organic materials include halogenated and phosphorous compounds. Inorganic flame retardants have poor effectiveness, lack of toxic byproducts, and they are also low in cost. That is why high level of materials are used for incorporation to reach the required flame-retardant level is required. This material can cause detrimental properties to other qualities of the polymer. Halogenated compounds are effective flame retardant but high temperature conditions are required to initiate the radical-trapping. Polyurethanes might not have as high temperature to start the activity of radical-trapping. Halogenated compounds also states hazardous because of the emission of the gas in the form of hydrogen halides. Continuous work is done to make such kind of flame-retardant product which does not include all these side

effects. Compounds containing organic phosphorous are supposed to be very effective nontoxic flame-retardant additives [43].

7.6 New Innovations and Future of Polyurethane Coating

Most useful class of polymers is polyurethanes. Polyurethanes have numerous required properties that might be exploited by researchers for manipulative coatings. From vast range of applications, examples consist of:

- the usage of polyurethanes in clear coating for the glass,
- in aliphatic single-pack roof coatings,
- as the key binder in anticorrosive paint,
- as a scrap tyre binder for sporting surfaces,
- as an excellent quality, light-stable line marking paints,
- as encapsulants for weathered asbestos.

New isocyanates are commercially accessible now and they contribute a lot in the development of the technology of polyurethanes. Polyurethanes have good abrasion, cure well at low temperature, impact resistance, and excellent resistance to chalking. Aromatic polyurethanes are less expensive compare to the aliphatic polyurethanes. Because of this fact, this is more usual to have aromatic polyurethanes or epoxies, particularly used in base or tie-coats and use in primers [44].

7.6.1 Development in Biomaterials

The initial catastrophe failure of constituents, for example silk, metal, ivory, glass, and nylon brought significant principles into emphasis: thrombogenicity and durability. Then, focus was engaged at inert substances that slightly interrelate with blood and tissue. Polyethylene terephthalate and expanded polytetrafluoroethylene are presently the standard biomaterials of prosthetic vascular grafts. By the use of large period of time, properties that are examined state that both polyethylene terephthalate and expanded polytetrafluoroethylene grafts, exposed to achieve well at diameters of 6 mm, but neither substance has been appropriate for small-diameter of 4 mm applications. Biodegradable polymers might establish a momentary scaffold by which tissue in growth *in vivo* ultimately substitutes the prostheses and left behind a whole biological vascular conduit. The emergence of tissue-engineering technology has concurred the progress of a novel

biologically viable vascular substitute possible, and it has been proved to be the possible solution for small-diameter vascular grafting.

7.6.2 Future of Paint Industry

While in the formation of high-quality coatings, because of the variable properties and diverse formulation, polyurethane binders are the preferred choice. A mature industry: coating and paint industry undergoes continuous change in the approaches/technologies. In the last 10 years, some market places, for example, automotive, have governed 95% change in the synthesis and composition of coating and paints, which they are used to apply on their products. In 2011, the worldwide marketplace share of polyurethane coatings, apart from architectural paints, can be predictable at nearly 15%. The configuration and medicine chemistry related with “compliant” coating technology are further discovered with respect to UV radiation curable coatings, high solids (solvent borne) coatings, powder coatings, and waterborne coatings. For future research and development, definite areas are being targeted. Polyurethane coating have the advantages of mechanical and chemical resistance and excellent weathering characteristics. These properties of the polyurethanes coating enable them to gain a leading market share in both the aerospace and auto refinish industries [45].

7.7 Conclusion

Polyurethane adhesives as a class can no longer be perceived as new raw materials. From a base of 217 million pounds, double-digit growth can no longer be expected. Even more significant growth of this industry will continue. Formulators are taking advantage of the tremendous flexibility of urethane chemistry in designing new adhesive products. Specialty niches such as waterbornes and reactive hot melts, for example, will continue to emerge and fuel growth. Exciting times lie ahead for innovative formulators of polyurethane adhesives.

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Electroactive Polymer Nanocomposite Coating

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Abstract

Shape memory polymers may relax to regain original shape through external heat, light, electricity, moisture, or pH. Electroactive polymers have capability to exhibit change in size or shape stimulated by electric field. Conducting polymers have been employed as successful electroactive materials. In this chapter, electroactive polymer coatings have been discussed regarding fabrication, features, and applications. Electroactive polymer coatings have shown light weight, high electrical conductivity, high durability, large bending deformation, rapid response, high stability, low voltage operation, high actuation, and anti-corrosion performance. Electroactive polymeric nanocomposites have been developed using conducting/nan-conducting polymers and nanoparticles such as graphene, carbon nanotube, and other nanoparticles. Electroactive nanocomposite actuator coatings have also been formed by incorporating nanoparticles in polymeric matrices. Electroactive materials have high surface area and exceptional electrical conductivity owing to beneficial interfacial interaction between electrons of conducting polymers and nanocarbon. Electroactive polymeric nanocomposite coatings exhibited homogeneous distribution of nanocarbon, high electrical conductivity, and electroactive shape recovery performance at low nanofiller loading. These nanocomposite coatings also possess mechanical and thermal stability. Electroactive polymers and nanocomposite coatings have been found beneficial for anti-corrosive coatings, antibacterial coatings, and films for sensors and actuators. More extensive research attempts are recommended to discover future applications of these coatings.

Keywords: Conducting polymer, nanocomposite, coating, actuator, nanofiller, conductivity, anti-corrosion, antibacterial

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8.1 Introduction

Shape-memory polymer can be deformed and fixed into temporary shape, and permanent shape is usually recovered by external stimulus of electricity, heat, light, magnetic field, pH, moisture, etc. Shape memory polymers have gained significance in myriad of fields such as aerospace, aircraft, engineered structures, and biomedical. Conducting polymers are eminent high-performance materials owing to desired conductivity, strength, heat stability, and chemical inertness performance [1, 2]. Various conducting polymers have been exploited as electroactive materials such as polyaniline, polypyrrole, polythiophene, and derived forms [3, 4]. Electroactive polymers particularly have electroactivity better than their mechanical properties and thermal stability. Polymers have also been reinforced with conducting nanoparticles such as carbon nanotube, graphene nanosheets, and inorganic nanoparticles to attain electroactivity [5, 6]. In the fabrication of electroactivate shape memory nanocomposites, the shape-memory effect may depend on nanofiller content and surface-modification of nanoparticles. Conducting electroactive coatings have been used in superior corrosion protection of metallic substrates [7]. Electroactive polymeric nanocomposites have also been applied in microelectronics, sensors, e-textiles, and biomedical relevance [8–10]. Moreover, the electro-activate actuator coatings have been employed in controlling microaerial vehicles.

This chapter quotes recent developments in electro-induced shape recovery polymer coatings. In shape memory polymers filled with conducting nanofillers, electricity has been used as stimulus to enable resistive actuation. The electric triggering of shape memory polymer and nanocomposite coatings enlarges their technological potential from anti-corrosion to sensing and biomedical applications.

8.2 Electroactive Polymer

Electroactive polymers are materials proficient of transferring their size, shape, or volume when exposed to external stimulus of electric field [11]. The electrical energy is usually applied to mechanically deformed materials. The electrostatic forces in these polymers may lead to electromechanical change in shape of materials. Electroactive polymers are also named as shape memory polymers having low cost, lightweight, facile processing, fracture tolerance, easy programming, and high shape recovery ratio. Recently, the electro-activated shape memory polymers and composites

have gained significance [12]. Electroactive materials with fine degradability, biocompatibility, robustness, and electroactivity are preferred. In electroactive polymeric nanocomposites, various types of nanofillers have been used. Incorporation of reinforcements may affect the conductive properties of these materials. The mechanisms of electrical conduction and shape recovery of electroactive polymers have been explored [10]. Electroactive polymers, composites, and nanocomposites have been employed in sensors, actuators, flexible circuits, and energy harvester [13]. Electroactive composites have usually fast response, bear large activation stresses, and may induce displacement under direct current (DC) activation, compared with the electroactive polymers. Moreover, electroactive nature of nanoparticle-reinforced materials has found widespread applications in tissue engineering and drug delivery. Electroactive nanocomposite materials with enhanced flexibility, scalability, advanced electrical field, and manufacturing possibilities have been researched [14, 15]. In scalability of these materials, potential errors dramatically increase to comply with the durability of architectural standards.

8.3 Electroactive Polymer and Nanocomposite Coating

In electroactive polymeric nanocomposite, the most important material used is conducting polymers. The electroactive polymeric nanocomposites have also been produced using non-conducting polymer and conducting nanofiller materials such as carbon nanotube, graphene, inorganic oxides, and metal nanoparticles [16, 17]. The electroactive nanocomposites have enhanced processability, electrical conductivity, specific capacitance, and mechanical strength [18]. Common conducting polymers used in electroactive materials are polyaniline, polypyrrole, polythiophene, and their derivatives [19]. Polyaniline (PANI) is an important conducting polymers with exceptional processing, electrical, optical, and environment features [20]. Shiri *et al.* [21] combined p-type conducting polymer with Gadolinium oxide nanoparticles through electropolymerization. The electroactive nanocomposite was used as supercapacitor electrode coating materials with specific capacitance and specific energy of 300 Fg^{-1} and 41.66 Whkg^{-1} , respectively. Electroactive polymer-based actuators have also gained attention in micro-electromechanical systems (MEMS) and biomedicine. Ru *et al.* [22] developed ionic electroactive polymeric actuators having large strain under low-voltage stimulation. Polymeric

nanoporous carbon nanotube coating was fabricated with high conductivity of 1,000–2,000 S/cm. Actuator performance was evaluated in terms of generated strain of 1.26% and stress of 5.27 MPa. The increase in voltage by 1 V had enhanced the strain and stress by 0.336% and 1.407 MPa, respectively. Such actuators can be used as promising candidates for artificial muscles. The actuator has porous hierarchal structure to support electrical and mechanical properties for improved electrochemical and electromechanical properties. Prabhakar *et al.* [23] developed polyurethane coated with polyaniline and silver nanoparticle (AgNP) nanocomposite for biomedical application. The electroactive PANI/AgNP coating has shown reduced inflammatory response in human cells. The materials have shown potential application in electrochemical biosensors [24, 25]. The electroactive PANI/AgNP coatings have enhanced biocompatibility than the neat polyurethane. A major application of electroactive coatings is for the corrosion protection. Electroactive polymer nanocomposite coatings have enhanced the anti-corrosive abilities with the addition of nanoparticles, compared with the neat conducting polymers. Hence, electroactive polymeric nanocomposite coatings have superior conductivity, robustness, capacitance, and anti-inflammatory response compared with the unfilled polymers.

8.4 Applications of Electroactive Polymer Nanocomposite Coating

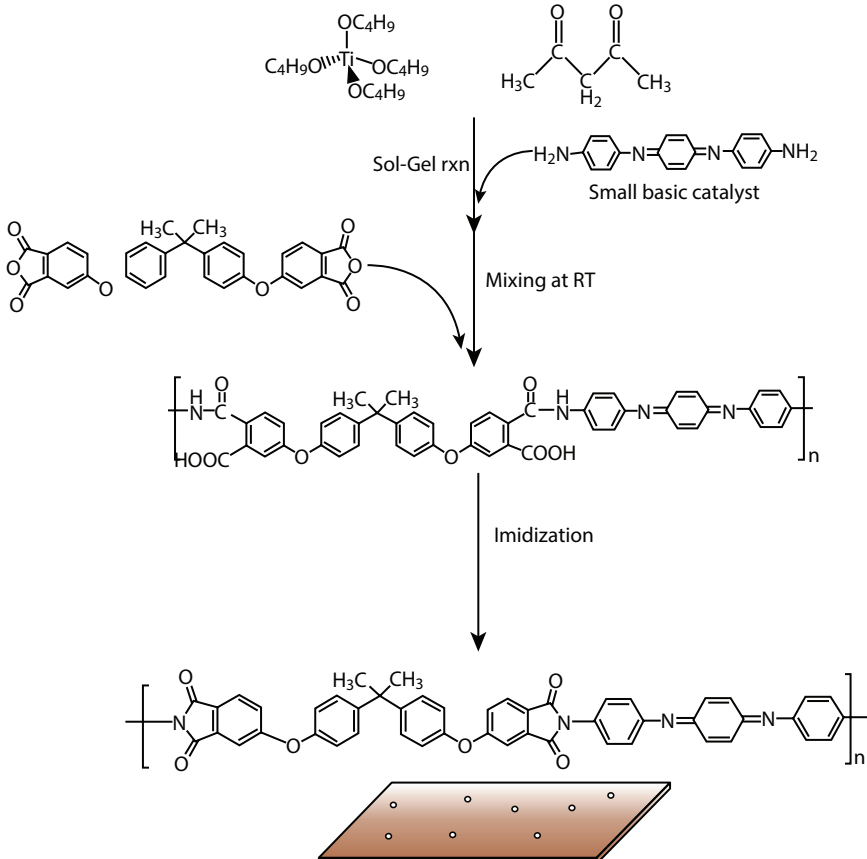
8.4.1 Electroactive Anti-Corrosive Coating

Electroactive polymer and nanocomposites have been employed as anti-corrosive coatings [26, 27]. Electroactive PANI, polyimide, and epoxy resin coatings have been developed on metallic electrodes and studied for corrosion protection [27, 28]. Mechanism of anti-corrosion of conducting polymers for underlying metal against the attack of aggressive species has been explored [29]. Huang *et al.* [30] prepared electroactive polyimide/nanoclay nanocomposite coatings for corrosion protection. The coating was formed on cold-rolled steel (CRS) electrode. The electrochemical measurements such as corrosion potential (E_{corr}), polarization resistance (R_p), and corrosion current (I_{corr}) were investigated in 5 wt.% NaCl electrolyte. Table 8.1 shows that nanocomposite coating with higher nanoclay content had higher corrosion potential. The polarization resistance of highly loaded coating was also much greater than the uncoated CRS. Gas barrier properties and redox behavior of coatings were studied by gas permeability

Table 8.1 Electrochemical corrosion measurements of the materials [30].
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Sample	E_{corr} (mV)	R_p ($k\Omega\text{cm}^2$)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
CRS	-1020.9	2.47	9.14
Polyimide	-807.7	17.30	2.53
Polyimide/nanoclay 0.004 wt. %	-664.9	36.67	1.89
Polyimide/nanoclay 0.012 wt. %	-528.5	69.99	1.09

analysis and electrochemical cyclic voltammetry. The coatings possess excellent oxygen resistance and anti-corrosion properties. Yuan *et al.* [31] designed multifunctional coatings of polyaniline/functionalized carbon nanotube (PANI/fCNT) and ethylene tetrafluoroethylene (ETFE). The coatings revealed anti-corrosion, self-cleaning, and anti-wear properties. The ETFE coating with 6wt.% PANI/fCNT had superamphiphobic property with contact angles of 159° – 167° . The superamphiphobic properties were retained upto 90 days in 3.5 wt.% NaCl. Chang *et al.* [32] prepared anti-corrosion electroactive polyimide/graphene nanocomposite coatings. The well-dispersed graphene nanosheets in coatings hindered the gas migration and corrosion resistance exponentially. Huang *et al.* [33] formed coatings of epoxy/amino- SiO_2 nanocomposite with electroactive amino-capped aniline trimer (ACAT). Corrosion potential, corrosion current, and electrochemical impedance spectroscopy studies on coatings were performed in 5 wt.% NaCl electrolyte. Electroactive epoxy/amino- SiO_2 /ACAT coatings have shown enhanced oxygen barrier properties and corrosion resistance. Weng *et al.* [34] designed electroactive polyimide- TiO_2 (EPT) coatings. Increase in TiO_2 concentration revealed higher corrosion protection of these coatings. Electrochemical corrosion measurement of cold-rolled steel electrode coated with EPT was measured in 5 wt.% NaCl electrolyte. Figure 8.1 shows synthetic procedure of EPT. Firstly, poly(amic acid) solution was formed using 4,4'-(4,4'-isopropylidenediphenoxy) bis(phthalic anhydride). Figure 8.2a depicts redox catalytic properties of EPT. The mechanism was based on the formation of passivation protective metal oxide layers. The corrosion protection performance of EPT was found similar to the reported PANI coatings [35]. Figure 8.2b shows diffusion pathway of oxygen gas in the EPT coating formed on CRS electrode. The EPT nanocomposite coating with 0.5 wt.% TiO_2 revealed 21% reduction of O_2 permeability. Further, increase in TiO_2 loading resulted in more



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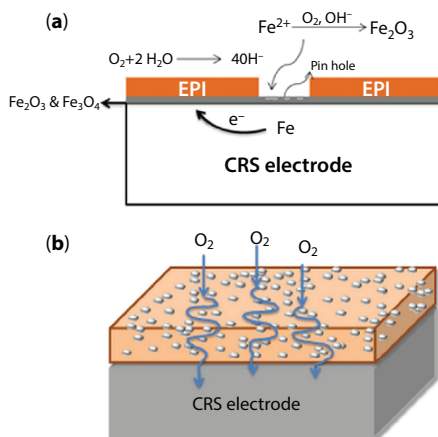


Figure 8.2 Schematic diagrams of (a) mechanism of CRS passivation by EPT coatings and (b) diffusion pathway of oxygen gas in the EPT [34]. Reproduced with permission from Elsevier.

electroactive antibacterial properties [40, 41]. Khan *et al.* [42] developed conductive bio-hybrid coatings of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonic acid) (PEDOT:PSS) with chitosan and polyvinyl alcohol (PVA). The biocidal potential of neat electroactive PEDOT:PSS, nanocomposite coatings, and chitosan were tested against *S. aureus* and gram negative *E. coli* bacterial strains using disk diffusion method (Figure 8.3). Pure PEDOT:PSS had no antibacterial activity against bacterial strains. The prepared bio-hybrid coatings were effective against

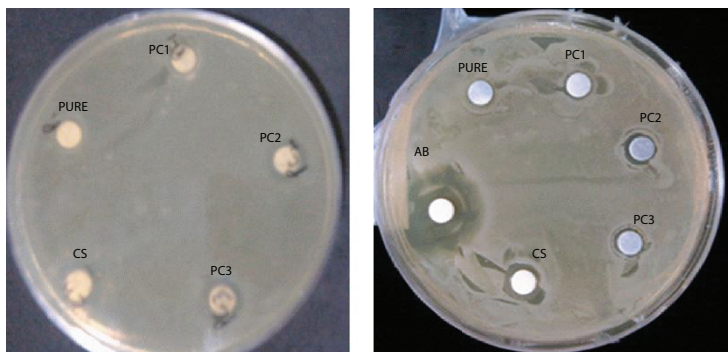


Figure 8.3 Inhibition zone of chemically synthesized pure PEDOT: PSS, bio-hybrid films PC1 (1:1), PC2 (1:2), and PC3 (1:3), and chitosan (CS) against gram positive bacteria and *S. aureus* [42]. Reproduced with permission from Elsevier.

gram positive bacteria. The bio-hybrid coatings with chitosan has much enhanced antibacterial property against *S. aureus* and gram negative *E. coli*. It was found that there were electrostatic interactions between amino groups of chitosan and anionic microorganisms leading to enhanced antibacterial effects. Gharibi *et al.* [43] designed polyurethane/siloxane-based electroactive wound dressing membranes. The physicochemical, mechanical, electrical, and biological properties of the coatings were found effective. Zhao *et al.* [44] formed poly(ethylene glycol)-*co*-poly(glycerol sebacate) as antibacterial, anti-oxidant, and electroactive dressing for cutaneous wound healing. The materials had shown good self-healing, biocompatibility, antibacterial activity, adhesiveness, conductivity, and electroactivity features. The electroactive dressing also possesses *in vivo* blood clotting capacity. Ahmed *et al.* [45] fabricated electroactive polyvinyl-*N*-carbazole (PVK) and single-walled carbon nanotube (SWCNT) coatings. The antibacterial effects were determined for *E. coli* and *Bacillus subtilis* strains. The hydrophobic and electrostatic interactions between conducting polymer and microorganisms synergistically inhibited the growth of microorganisms and bacterial strains and enhance the actuation performance.

8.4.3 Electroactive Coating for Sensors and Actuators

Polymer nanocomposites have been exploited in chemical and biological sensors [46, 47]. Polymers reinforced with nanoparticles such as graphene, carbon nanotube, and metal nanoparticles exhibited high surface area, electrical conductivity, and fast electron transfer rate. These nanocomposites have been employed in electronic sensors, biosensors, immunosensors, and electrochemical sensors. Recently, electroactive polymer nanocomposites have been employed in coatings of sensors and actuators. Kulkarni *et al.* [48] reported polyaniline wrapped-multi-walled carbon nanotube (PANI-MWCNT) coatings through *in situ* chemical polymerization. The synthesized nanocomposite coating was sensitive towards pH change of the solution. The materials were potentially important for optical pH sensing. Mahmoudian *et al.* [49] developed polypyrrole coating on nanospherical platinum. The coated materials was sensitive towards the mercury ion concentration in the range of 5 to 500 nM. Ionic or electrolytic polymers have also been studied as actuators. The driving force for such a actuators is the volume change due to oxidation/reduction reactions [50]. Such electroactive polymers have been utilized in artificial muscles. Conducting and electrolytic polymer coatings have found potential for sensors and actuators [51]. Their use in sensors and actuators depend on inherent conductivity

[52]. Park *et al.* [53] prepared poly(vinylidene fluoride) (PVDF) and carbon nanotube (CNT) nanocomposite coating on indium tin oxide (ITO). The coatings were investigated for self-sensor and micro-actuator applications. Figure 8.4 shows morphology of the surfaces of nanocomposite and ITO coating material. The ITO coating had non-entangled morphology compared with the nanocomposite. Figure 8.5 shows the effect of increasing nanofiller content on the activation displacement of nanocomposite and ITO coated material. With the increase in nanofiller content from 3 to 12 wt.%, the electrical conductivity and actuator displacement of ITO

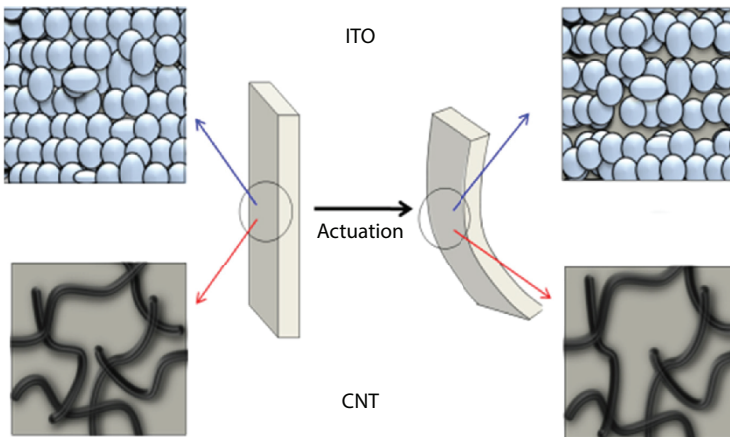


Figure 8.4 Sketches of proposed changes in layer morphology during actuation [53]. Reproduced with permission from Elsevier.

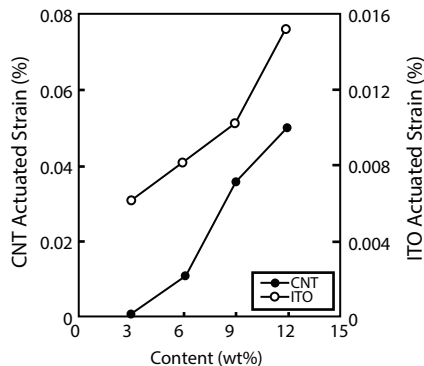


Figure 8.5 Actuated strain vs. nanofiller content for PVDF/CNT and ITO coated layers [53]. Reproduced with permission from Elsevier.

coated material were enhanced compared with the nanocomposite [54, 55]. Hence, PVDF/CNT nanocomposites coatings have shown high performance for self-sensors and micro-actuators.

8.5 Future and Summary

Electroactive polymer and nanocomposites have gained increasing academic and industrial interest. Development and characterization of new conducting polymers may bring about advancements in the field of electroactive materials [56, 57]. In this regard, conducting polymers as well as ionic/electrolytic polymers have been identified as electro-actuated materials. Both the conducting polymers and ionic polymers have been used as electroactive coatings. In the case of conducting polymers, transport mechanism is electronic in nature. Progress in this field depends upon the identification of new derivatives of polythiophene and polyaniline with enhanced electrical conductivity. Incorporation of conducting polymers in polymers may also enhance the electrical triggering and anti-corrosion performance of coatings. Advancements in ionically conducting polymers can be achieved through the dissolution of salts in macromolecular solids. For example, poly(ethylene oxide) has been mixed with lithium salts to get electroactive polymer. Similarly, other water soluble polymers can be mixed with salts. Amalgamation or modification of conducting polymers with biomaterials have led to unique actuation properties of coatings [37]. In this regard, new bio-hybrids had synergistic properties of conducting polymers and biomaterials. Field of electroactive polymers and nanocomposites needs to be researched to get high performance self-sensors and micro-actuator coatings.

This chapter describes various aspects of electrically triggered shape memory polymers and nanocomposites. The recent advances in this field depends upon the nature of polymer, fabrication strategies, conductivity properties, easy programming, fast recovery rate, and resistance to large activation stresses. Interaction between electro-activated polymer coating and substrate has also enhanced the anti-corrosion properties. Electroactive antibacterial properties of coatings have also been explored. Field of sensors and micro-actuators based on electro-activated polymer coatings were found to exhibit superior performance than non-electroactive polymers. Future advancements in the field of electroactive shape memory polymeric materials may enlarge their technological potential in several concealed high-performance areas.

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Conducting Polymer Coatings for Corrosion Resistance in Electronic Materials

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Abstract

Corrosion of the electronic material is the critical problem for many applications. Hence the researchers focused for the development of corrosion resistance coating material which has multifunctional properties such as electronic conductivity, better mechanical strength, more flexibility in the use and synthesis. In general, the polymers were used as coating material for the electronic and other materials. In the polymer types, the conducting polymers (CPs) got importance as it conduct electricity and have good multifunctional characteristics. Significantly the CPs such as PANI, PPy, and PEDOT:PSS and their derivatives are used as coating material to inhibit corrosion. In this paper we summarized the CPs and their composites which have used for the corrosion resistance.

Keywords: Conducting polymers, corrosion, coating, PANI, PPy, PEDOT

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9.1 Introduction

The corrosion is the one of the source of the damage of the electronic materials and related peripheral electronic materials. Some of the few materials which are used in these days to fabricate electronic devices are more sensitive; hence, the materials affected themselves for the corrosion by oxidation. The demolition or worsening of electronic devices because of the nature and surroundings reaction is maybe referred as corrosion [1]. In general, the protection of the electronic materials from the corrosion did by the painting and coating of the organic materials (see Figure 9.1). The corrosion depends on the ability of coating which protects the metal surface when the metallic surface damaged in its life period. In recent days, conducting polymers for coatings are the one of the choice to protect electronic material defects from the corrosive nature due its conductivity and flexibility [2].

The corrosion environment for the electronic materials mainly happened by two basis that are first one is materials corrosion by itself and exterior world. Generally, hermit cavities are used for package or cover surface of the electronic materials to minimize first-type corrosion, in this case the air filtration process is used for the substances which are influenced

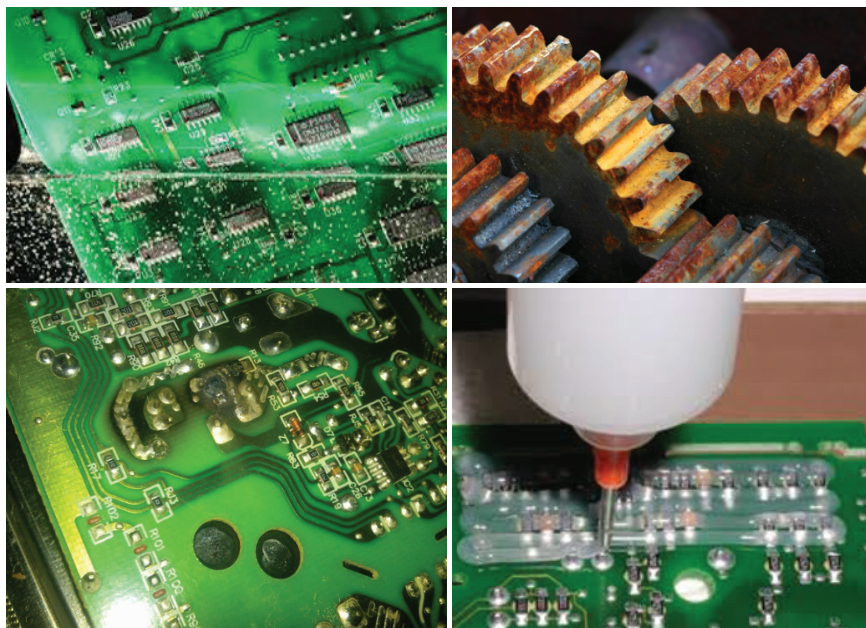


Figure 9.1 The photographs of corrosive electronic materials and removal process.

by corrosion due to external sources. The substances or materials which are exposed by external environment were well defined until now, even this substances corrosion practiced by photoactive packaging process [3]. The electronic devices mostly, in practice level of packaging restrictive packages, encapsulates and protective painting used to remove which the peripherals from internal and external world are available to degrade performance. These phenomena are also true for the components like printed boards, connectors, optical transmitter devices, electronic chips, which are kept in substrates, and many other same kind of devices [4–5]. The packaging materials itself are exposed to a nature of whose source is external and internal sources. The low molecular weight organic compounds interacting are the part of materials which are derived by the internal source due to its volatility and mobility the materials can diffuse on the metallic surface using other organic materials broadly used in electronic equipment fabrication [6]. Traegere *et al.* [7] made reviewed about the substances which are out gassed from organic materials those which were used in electronics. The researchers Weshler *et al.* [8] have discovered a number of components in insulation and corrosion resistance material. Those are present in both the vapor and condensed phase electronic machinery. On the other hand, the humans or atmosphere (external sources) made corrosion of the electronic substances. Gill and co-workers [9] have investigated and listed some compounds which are found in atmosphere with vapor pressure in specific range from internal.

In the exterior environment, there were many studies involved about corrosion studies. The researchers Vernon *et al.* [10] identified the products related to the sulfur dioxide and its oxidation states and humidity are the common responsible for corrosion in exterior world. He also gave results as the rate of corrosion increases with the absorption of humidity by material surface. The most materials have relative humidity value in the range of 70% to 80%. Rice *et al.* from United States studied rate of corrosion for the materials such as silver, nickel, cobalt, copper, and iron in different circumstances and concluded that the silver has low corrosion rate than the other. The coating to the materials depends on the corrosion which was happened by the interactions with surrounding environment. In the case of environmental interactions, generally the electronic materials get corrosion from the air interaction and some other devices more responsive to the dampness and ionic pollutant. All the elements such as metals and semiconductors which were used in the fabrication of electronic devices all are thermally active and oxidized easily at temperature 20°–40° (near in the room temperature). If we try to control the corrosion by decreasing oxidation through the self-limiting or restrained, then the materials

go destructive. However, the electronic devices need the thin oxide films synthesized by the corrosion controlled conditions. In the periodic table, 3rd group and 5th group semiconductors which were commonly used for electronic materials significantly look as complex as the problems are arise at the synthesis of corrosion restrictive films of the 3rd and 5th group elements in the semiconductor technology and devices [11].

On the second major cause of the corrosion is interaction of water and other constituent. The attending of the moisture can give electrochemical effect; hence, the electronic devices performance surely be slow down or damaged permanently. The oxidation formation and the oxidation rate depend on the humidity in the atmosphere so it leads to deformation of structure and changes happened in the properties of electronic materials. The main components and connectors of electronic gadgets keep safe with the coating of noble metals like gold and platinum etc. The corrosion which comes from the gold coating gets creep in the surface of materials which leads to high contact resistance. Because the moisture is present, the atmosphere can increase the copper mixed oxide with sulfide in the case of gold-coated copper materials in the sulfide environment. Generally, in the case copper-gold alloys, the nickel barrier layer restrains the interdiffusion by eliminating pores and extents copper on contact surfaces between the copper and gold [12].

Generally, the corrosion constrained by the coating by the external sources such as polymer coating and sealing with respected sources. Commonly, the coating is referred as the painting on the surfaces of the electronic components, envelope with the shielding materials like the organic or inorganic elements. However, the electronic peripherals are coated with the polymers that are natural polymers or synthetic polymers. Nowadays, conducting polymers are used as the purpose of the coating due its electric conduction and flexibility [13]. Apart from the conducting polymers, there was natural polymers such as natural rubber or polyvinyl chloride, silicon, pollsters, etc. However, using the conducting polymers gives more advantages as it possesses conducting nature.

9.2 Conducting Polymers

9.2.1 Polyaniline (PANI)

Guptha *et al.* [14] prepared PANI-lignosulphonate (PANI-LGS) binder for the corrosion protection of aluminum 2024 alloys by chemical oxidative polymerization method and its performance is analyzed first time. They

found the low content of PANI-LGS shows less dispersibility instead of high volume fraction of particles eliminates from the particles agglomeration. The maximum value of coating obtained at minimum PANI-LGS system and high volume microstructure were observed from the analysis with best adhesion after immersion then other coating formulation. The researchers also revealed that PANI distribution reduced the water and oxygen as a result the protection of coating increases effectively. The formation of complex of aluminum-sulfonate as giving the dependence where it required and also the thick layer of the oxide increases the corrosion protection. The authors also presented a conceptual chart in their study. When the aluminum alloy dipped into the corrosion environment the PANI-LGS system releases the doped LGS ions to prevent from the corrosion.

Ayad *et al.* [15] synthesized PANI ammonium hydroxide complex using chemical deprotonate method and PANI sulfamic, citric, succinic, and acetic acid complexes through the reprotonate method. The PANI oxidation ranges were estimated using the UV-Visible spectroscopy and the absorbance rate founded in between 360 nm and 438 nm. They analyzed using IUPAC procedure as taken PANI absorption as basis in the emeraldine state the doping concentration was estimated. The varied PANI concentration found as for sulfonic acid is 0.27, for succinic acid is 0.18, for citric acid 0.15 and for acetic acid is 0.13. The polarization calculations took for the estimation of corrosion nature. They terminated results as polarization resistance and productivity of corrosion seems to be as variation of PANI concentration. The increment of PANI concentration increases the polarization resistance then these results support the increment of coating concentration. The composite coatings gradual decreases of the polarization resistance values are observed after 300 hours. While for 150 hours, base coating demonstrates high decrement value of polarization; hence, it leads to the coating delimitation. From the above information, we can conclude that the PANI mixer coating decreases the delaminating.

Satyanarayana *et al.* [16] studied PANI tincture coated steel material in NaCl and HCl solution through EIS (electrochemical impedance spectroscopy). The studies reveal the experimental results as the wide corrosion resistance observed by coating PANI pigment coating in the acidic and neutral state. The studies indicate clearly the PANI coating highly protective in acidic medium.

Olad *et al.* [17] synthesized the Zn nanoparticles incorporated PANI composite through the *in situ* polymerization process by energetic stirring process. The prepared PANI/Zn nanocomposite is used to study the electrical conductivity. The studies showed that the prepared PANI/Zn nanofilms conductivity is better than the pure PANI conductivity. The electro-active

nature of PANI/Zn is confirmed through voltammetry. The more importantly, the corrosion study results are given as the anticorrosion of PANI/Zn nanocomposite on the iron materials clearly with kinetically and thermally as good as than the PANI.

Zhu *et al.* [18] synthesized graphene oxide and PANI composite through the *in situ* polymerization. The researchers observed that aniline polymerized graphene oxide shows water dispersibility. The GO/PANI composite coating is prepared and coated on mild steel for the corrosion studies. In the acidic environment (NaCl) using electro impedance spectroscopy and OCP, the corrosion properties are studied. The results are concluded as the PANI and GO have shown very good anticorrosive nature. The comparative anticorrosion study has made between the WEP composite and PANI/GO coated WEP composite, the researchers noticed that WEP/PANI/GO was shown better anti-corrosion than the WEP composites. The PANI works as electroactive protector and the GO sheets protected from the water obstacle performance.

Yanga *et al.* [19] synthesized nanofibers of PANI using conventional, interfacial polymerization and direct mixed reaction methods in sulfuric acidic media. The pure PANI nanofibers have uniform surface properties in the range of nanometers. The electrochemical corrosion studies of nanofibers which are synthesized through direct mixed reaction have shown very good corrosion protection for the kind of steel. As a whole, the studies revealed that PANI surface properties and nanostructure well anticorrosion achievement.

Paula *et al.* [20] synthesized the PANI microspheres by incorporating of the methyl methacrylate and butyrylate, acrylic acid nanoparticles through the two-step process such as emulsion polymerization and core-shell formation on the aniline monomer. The prepared P (MMA/BA/AA)/PANI film-forming properties attained with acrylic waterborne formulations. The two-step synthesis process makes possible to get well semiconducting properties; this was confirmed by the UV-Visible spectroscopy and conductivity measurement. The corrosion properties were checked with the help of electrochemical impedance spectroscopy and also mechanical and thermal stability of the films looks better values. Finally the corrosion properties were analyzed as the passivation effect stimulated due to the incorporation of the PANI and instructed the enhancement protection to carbon steels.

The acrylic ester grafting epoxy (A-g-EP) with eCOOH functional groups was fabricated by the researchers Zhu *et al.* [21]. Then, the PANI and A-g-EP composite was got by via oxidation polymerization and *in situ* polymerization techniques of aniline on A-g-EP macromolecular chains.

The grafted epoxy and PANI-A-g-EP composite solution with 30 wt% concentration on the mild steel with the thickness of the coating was controlled to 25–30 μm . The PANI has served as the creating the conduction bridges in between A-g-EP chains it results the bupolaron existence so that the possibility of antistatic properties of PANI-A-g-EP revealed. The anti-corrosion properties of PANI-A-g-EP composite coating are revealed by the electron transmission and passivation catalysis.

Zhua *et al.* [22] reported new method that simultaneous annealing conditions for the preparation of RGO- Fe_3O_4 -PANI tracer nanocomposites should be formally reduced with aniline monomers on GO nanosheets but without the use of a secondary reducing reagent. And then, aniline RGO can be used in polymerization. π - π electronic interactions between RGO and PANI to promote metal passivation effect and also p-n junction between PANI and Fe_3O_4 to improve anti-corrosion performance. When 0.5 wt% of RGO- Fe_3O_4 in PANI nanocomposites were added to the water-borne acrylate amino solution, the resulting coating showed excellent anti-corrosion properties. The mechanism of counteraction of RGO- Fe_3O_4 -PANI nanocomposites has been revealed to be an effective physical barrier due to the layered assembly of the microstructure. Increased passage catalysis and p-n junction have been established, which allows only one-way electron transport and limits oxygen depletion, thus effectively improving the corrosion resistance.

9.2.2 Polypyrrrole (PPy)

Tunc *et al.* [23] prepared PPy film on the surface of the copper and brass metal through electrochemical method. The quantity of the copper ions incorporated at the time of synthesis to alter the PPy polymer film. The anticorrosion result analyzed as the PPy film could contribute protection in opposition to corrosion of brass and copper even at acidic environment at given period. Clear anticorrosion mechanism that was discussed by authors indicates the importance of the PPy for the corrosion resistance. However, the corrosion measurement revealed the fact that the coating of PPy is good on the copper then the brass.

Attarzadeh *et al.* [24] made an appealing study of the PPy polymer. The scientists used the Saccharinsodium to incorporate in the PPy through the electrodeposition for the coating of steel. At the time of synthesis the electro-deposition was varied by changing the inductance when the saccharin introduced then the maximum polymerization potential were observed. These PPy coatings expressed very good anti-corrosive properties. Interestingly, on the morphological properties the smooth surface was

noticed at the saccharin concentration 0.5 g/l and it indicates the very good anti-corrosive nature of the PPy conducting polymer.

There were also some studies which related to the two or more conducting polymer contribution for the corrosion resistance. For example, Gouri *et al.* [25] created the PANI and PPy mixer coating on the surface of the aluminum substrate via electrochemical deposition with the help of the oxalic acid as a electrolyte. In the periodic voltammetry, an anodic peak is presented near 0.15 V in the minimum short time; the presented peak may due to the oxidation or adsorption of hydrogen atom. The composite coating periodic graphs also indicated an anodic peak power at 1.01 V versus SCE and the power peak of cathode near 0.7 V versus SCE. The FTIR analysis of coating reveals the composite coating of PPy structural vibration clearly. As well as the scanning electron microscopy images reflected the distinguished changes in the morphology of the polypyrrol and PANI coating.

The acidic nature of the surroundings is the main criteria for the efficiency of the coating polymers if the nature conditions are the acidic or base so that the corrosion also changes as per the instructions given by the

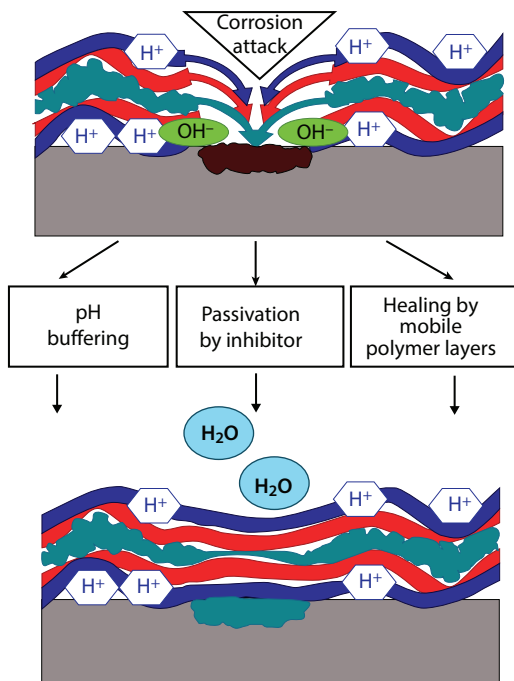


Figure 9.2 Influence of pH for the corrosion.

pH values (see Figure 9.2). The co-researchers of Jude *et al.* inspected this type of study. The researchers coated PPy on the steel rod at the conditions in both acidic and base through the polymerization of electrochemical. Fascinatingly iron oxalate layer formed in the acidic media with the potential of 1.2 versus SCE. As getting the positive value of the potential, the electrochemical polymerization of PPy raised on the substrate of passivation. The pH value of the reacted medium influenced y much on the passivation time and current density of the substrate. The passivation is spontaneous; the noncrystalline coatings were observed when the pH value is in maximum. Electropolymerization of PPy in the acid can only occurs afterword steel enclosed by the crystalline interphase.

Paliwoda *et al.* [26], group of scientists, study the MoO_{2-4} doped PPy conducting polymer and explained the corrosion properties. They observed clear inhibition effect on the delaminating process. Because of the wide pH value at the barrier of polymer and metal the PPy gets over oxidation. In the case of the Ppy/ MoO_{2-4} coating, this buffering effect cannot seem to be observed. The corrosion resistive ions which were protected by the leaching and pH changes were not affected as PPy releasing on coating. However, the power of circumstances during the cathode delaminating process in the release behavior, especially the effect of small easy incorporable cations and the elevated pH, needs additional examination.

Bereket *et al.* [27] coated Poly (5-amino 1-naphthol) (PANAP) film on the top of the ppy polymer film which is synthesized through the electrochemical synthesis (cyclic voltammetry). Hence, the polymer films that are single PPy film and multilayer PPy/PANAP film were introduced to the comparative corrosion study, the results shown that PPy/PANAP multilayer film as good as the single PPy film for the corrosion protection of mild steel which is immersed in saline liquid. It is found that, if the immersive time is increases, then the protective behavior of synthesized single layer and multilayer PPY films were extremes. This was studied by the properties of auto undoping when the synthesized layers were immersed in the corrosive solution. Finally, Poly (5-amino 1-naphthol) (PANAP)covered PPy multilayer shows better anti-corrosion properties because Poly (5-amino 1-naphthol) (PANAP) contains structurally reactive $-\text{OH}$ groups. The poly-pyrrole, alumina nanoparticles prepared through the polymerization process in the dihydroxybenzene presents. The prepared nanocomposite was used to corrosion protection process as filler in the corrosion soundings. The dihydroxybenzene developed the better coating adhesion for the Al alloy metallic surface. The presence of dihydroxybenzene improved coatings adhesion to Al alloy surface [28].

Prissanaroon *et al.* [29] investigated the corrosion protective material for the stainless steel. The group of researchers used PPy conducting polymer for the coating material of the steel rod. The dodecylbenzenesulfonic acid (DBSA) and oxalic acid taken as a co doping systems to synthesize PPy films through the electro deposition.

9.2.3 Poly(3,4-ethylenedioxy thiophene): Polystyrene sulfonate (PEDOT:PSS)

Anmona *et al.* [30] made PEDOT:PSS coated microelectrode of gold materials for the application of long-term stable interface. These types of materials can also be used as iodine etching process because the surface morphology is important in the point of view etching time and iodine concentration. When the gold electrodes etched in iodine solution for period of time the PEDOT:PSS thick film showed more stability. The PEDOT:PSS voltammetry activation procedure reduces polarization and impedance of electrode at the time of stimulation process. The researchers were concluding that this PEDOT:PSS development is promising coating material for the electrode for stability for long life period.

Pranti *et al.* [31] taken a step for the development of the efficiency of coating material with PEDOT:PSS in the form of composite or film. They designed a material which has long life period and sophisticated PEDOT:PSS film for neural application. The PEDOT:PSS micrometer layer has careful etching process and 100% stability aluminum electrode and the material evaluated by the ultrasonic studies and vitro studies. The neural simulative applications of PEDOT:PSS has shown good consistency. The PEDOT:PSS film electrochemical modifications by the voltammetry studies improve the characteristics of coated electrodes. The polarization of the material decreases it leads to improvement of charge addition capacity of the PEDOT:PSS electrode. The increment of signal to noise ratio shows the decrement of electrode impedance. These two phenomena reflects the PEDOT:PSS is a good coating material for aluminum electrode.

Tim *et al.* [32] scrutinized that the PEDOT is a required material to stimulate the electrode or whether the conduction of the PEDOT changes with respect into its lifetime. For this purpose, the group of scientists has taken the realistic test environment for the PNS functional properties like charge injection, pulse width, and constant frequency. The experimental results shown as PEDOT are a kind of essayist material to stimulate electrode with extreme properties then the platinum for the subchronic studies. In their

studies, they demonstrated how the coating fails or else conductivity is to be lost to suggest further studies of conducting polymer studies.

Zaid *et al.* [33] studied the neuronal sensing properties using the conducting polymer coating. They mainly focused on the charge density which is deposit greater than the 320 mC/cm^2 and which provide application in the neuronal stimulation and recording with PEDOT:PSS coating. The long period stimulation functions were observed in the case of PEDOT:PSS through maximum CIL and development in impedance at the time of biphasic stimulation. Conversely, for the implementations the material requires adhesion improvement. The biocompatible study of PEDOT:PSS coating expressed via unstencil and briefly of neurite outgrowth and neuronal possibility. However, there were no extra advantages observed from the macroporous than the moderate progress in electrochemical properties of PEDOT:PSS coating at the time of process.

Ghosh *et al.* [34] demonstrated the manufacture of highly durable electronic fabrics for flexible electromagnetic performance through an explicit method of dipping and drying. The conductivity of the PEDOT:PSS-treated PEG coated tissue was 51 cm every 1 dipping cycle (thickness of 0.38 mm). The increase in conductivity was dominated by the screening phenomenon (PEG 400) between PEDOT and PSS, which leads to the phase-separated structure and higher aggregation of crystalline PEDOT domains on the cotton fabric surface, confirmed by the smaller X angle and Lightning scattering study (SAXS). Efficiency was also increased with increasing coating cycles and a maximum of 46.80 dB reached just 20 dipping cycles. In addition, shielding and electrical performance was successfully increased with extended needle cycles of up to 82.7 S cm^{-1} and 65.6 dB . The special vodefiller mechanism that comes from 3D tomography effectively controls the electrical conductivity with shielding capability. High mechanical and chemical tolerance (thermal air aging, bending and turning, single-sided tape peeling test, prolonged exposure to sunlight, polar and non-polar solvent treatment, and boiling with water) Strength and durability proof (retention up to 95% EM Performance on each finished garment test).

PEDOT:PSS study showing clean steam electrodes coated with an electrically conductive polymer is stable for at least 7 weeks of continuous dipolar current stimulation, corresponding to a total of 4.2 billion dipolar current pulses. Analysis of impedance spectroscopy results showed no significant changes in impedance after this long-term evaluation. Additionally, volatile electrodes are not visible after soaking in PBS solution at body temperature for more than 10 months. However, impairment of the electrode sheath due to blackout in continuous motion shows the importance of stimulus

protocol stability to protect PEDOT:PSS active Layer. Overall, our results suggest that PEDOT:PSS coated electrodes are a good candidate for long-term recording and stimulation of chronically organized neural interfaces [35]. Ding *et al.* [36] prepared $x\text{VS}_2/\text{PEDOT-PSS}$ nanosheets through the methods such as solvothermal method VS_2 preparation and the immersion and freeze-drying process for the VS_2 incorporation into the PEDOT-PSS for the coating of anode materials in the LIB (lithium-ion battery).

9.3 Conclusion

The described studies are the considerable evidence for the use and importance of conducting polymers in the field of corrosion resistance of the electronic material. The Cps coated electrode shows better stability and maximum current density as well as anticorrosive nature. The CP, PANI, and its derivatives like PANI/Zn nanofilms conductivity and anticorrosive nature are better than the pure PANI. Whereas, the specified material like PANI and GO have shown very good anticorrosive nature. The PPy and their composite also show remarkable anticorrosive behavior for the electrodes which were synthesized different methods were revised. The PEDOT:PSS composite polymer widely used as coating material for the electronic devices.

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Polymer Coatings for Food Applications

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Abstract

In recent years, consumer demands, as well as obligatory regulations that have been passed by various national and international authorities, have pushed food manufacturers to produce tastier and healthier food products with longer shelf lives. Coating of food components is introduced as an effective approach to meet these demands and obligations. Biopolymers including polysaccharides, proteins, and waxes are the main ingredients used for creating edible coatings. They might be used individually or in combination. The coating process can be applied to a variety of food products ranging from very large objects to particles at the microscale or smaller. The term encapsulation is used for the latter. The objectives and techniques used for coating food products with large sizes are different from those used for encapsulating small-sized food materials. Dipping, enrobing, panning, and spraying are typical methods used for coating food products such as fruits and vegetables, meat and meat products, eggs, cheese, nuts, and fried food. While, spray-cooling, freeze-drying, emulsification, extrusion, and electrohydrodynamic atomization are the most common microencapsulation techniques. In this chapter, the main objectives, components and techniques used for coating food surfaces or encapsulating food components are discussed individually.

Keywords: Coating, encapsulation, hydrocolloids, waxes, shelf-life, polysaccharide, protein

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10.1 Introduction

The idea of coating food products is not new. Edible coatings have been utilized for centuries to enhance food quality and shelf-life. The first recorded use was in the 12th century in China on oranges and lemons to give them a glossy appearance and retard their senescence [1]. Later, in England, the shelf-life of meat products was extended using lard or fats. This process was named “larding” [2]. In the last 20 years, coating food has become one of the most important applications of polymers in food science and great research efforts have been devoted to this field [3].

According to Saleh and Guigon [4], the food coating process is defined as the covering of edible materials with a surrounding layer being composed of a single or multiple GRAS (Generally Recommended as Safe) components with specific functions. The coating process can be applied to a variety of food products ranging from very large objects to particles at the micro or nanoscale. The term encapsulation is used for the latter [4, 5]. The objectives and techniques used for coating food products with large sizes are different from those used for encapsulating small-sized food materials. In this chapter, the major objectives, main components, and the techniques used for coating food surfaces or encapsulating food components are discussed individually.

10.2 The Main Objectives of Coating Food Surfaces

The main reasons for coating food surfaces could include the following.

10.2.1 Controlling Mass Transfer

Undesirable mass transfer among the food and its surrounding environment can contribute to loss of food quality [5]. Moisture absorption, surface dehydration, flavor and aroma gain or loss, fat migration, and gas transfer are some of the most important problems occurring due to mass transfer across the food. Edible coatings on the food surface can prevent these problems by acting as a barrier against moisture, gas, and ultraviolet. They can also act as a mass transfer barrier among particles within a food system [6].

10.2.2 Carrier of Functional Agents

Edible coatings can act as a carrier for functional ingredients to food systems to improve their stability, quality, or shelf-life [7]. These functional

agents include antimicrobials, antioxidants, texturizers, nutraceuticals, probiotics, flavors, and colorants [8].

10.2.3 Physical Protection

Edible coatings applied on the food surface can protect them from physical damage caused by different mechanical forces applied during handling. This mechanical protection is especially important in fragile food products such as nuts, breakfast cereals, and snacks [3]. Han and Aristippos [9] reported improvement in the physical strength of cashew nuts against external forces with the aid of whey protein-based coating (Figure 10.1).

10.2.4 Sensorial Improvement

Usually, the food surface has a powerful impact on the consumers' first sensorial impressions. Therefore, the materials used for coating food can positively alter the organoleptic properties of the coated food [3]. Coatings can be used to give a glossy appearance or to provide a non-greasy or non-sticky surface when necessary [10]. They also can be used as an adhesive to add salt, sugar, colorants, seasonings, or flavors onto the surface of food products such as nut and confectionery [3, 11, 12].

10.3 Components of Edible Coatings

Forming a compact and uniform coating without pores and cracks on a food surface is important in preserving its quality. Moreover, a good adhesion should occur among the coating solution and the product surface [13].



Figure 10.1 Whey protein-based edible coating protects the cashew nuts from physical damage. The figure has been reproduced with permission from Han and Aristippos [9].

The effectiveness and functionality of an edible coating mainly depend on its barrier against water vapor and gases, which depends on the surface properties of the food, its storage conditions, and the chemical composition of the coating materials [14]. Biopolymers including polysaccharides, proteins, and waxes are the main ingredients used for creating edible coatings. They could be used individually or in combination [15].

10.3.1 Polysaccharide

Polysaccharides, due to their favorable functional characteristics, are the most versatile polymers used for food coating applications. They have an oil-free and colorless appearance. Most of them are neutral; while some of them are negatively charged. Polysaccharide molecules can interact together through hydrogen bonding and create a continuous coating network that can act as a barrier against gas and oil transfer [16]. However, the coatings made from these types of biopolymers are hydrophilic, and therefore, have poor moisture barrier characteristics [17].

Polysaccharides-based coatings have been utilized for enhancing the shelf-life of several food products. High-fat food products such as nuts, sausages, and fillets can be protected from oxidation with the aid of appropriate polysaccharide-based coatings [18, 19]. Moreover, the barrier properties of these types of coatings can retard the respiration rate of fruits and vegetables and protect them from dehydration [20]. They can also be used for encapsulating bioactive agents [21]. The most important polysaccharides used for this purpose include cellulose derivatives, chitosan, starch derivatives, alginate, carrageenans, and pectin.

10.3.1.1 Cellulose Derivatives

Cellulose is the most abundant natural biopolymer on earth. It is a water-insoluble linear polysaccharide composed of D-glucose units linked through β -1,4 glycosidic bonds. Methylcellulose (MC), hydroxypropyl cellulose (HPC), and hydroxypropylmethylcellulose (HPMC) are cellulose ethers obtained by partial substitution of hydroxyl groups in cellulose by ether functions. They are water-soluble and able to form a compact coating layer on the food surface [22]. These coatings have been reported to be tasteless, odorless, transparent, water-soluble, resistant to oil, with moderate gas, and moisture transmission properties [3]. They have been widely used for coating fruits [23, 24] or meat products [25, 26] and encapsulating bioactive agents [27].

10.3.1.2 *Chitosan*

Chitosan is the second most abundant natural biopolymer after cellulose. It is obtained by alkaline deacetylation of chitin. Chitosan coatings are characterized by having low oxygen permeability and excellent mechanical properties. Moreover, due to their cationic nature, they exhibit antimicrobial activity. Chitosan-based coatings have been widely used for enhancing the shelf-life of nuts [28], meat products [18, 29, 30], fruits and vegetables [31–33]. It has also been used as a delivery system for bioactive agents [34, 35].

10.3.1.3 *Starch and Starch Derivatives*

Starch is a mixture of amylopectin and amylose. Amylose is a linear biopolymer composed of α -1,4 anhydroglucose units; while, amylopectin is a highly branched biopolymer consisting of short α -1,4 chains linked by α -1,6 glucosidic branching points. Amylose is known to form continuous coating layers on the food surface, while coatings made from amylopectin have been reported to be brittle [36]. Starches and their derivatives have been widely used for coating cheese [37] fruits [38–40], bakery products [41], and encapsulating functional ingredients in food systems [42].

10.3.1.4 *Seaweed Extracts*

Alginates and carrageenans are two main seaweed extracts used for food coating applications. Alginates are linear biopolymers consisting of L-guluronic and D-mannuronic acid units; while carrageenan is a water-soluble polymer formed by alternate units of 3,6-anhydrogalactose and D-galactose joined by β -1,4- and α -1,3-glycosidic bonds [43]. These seaweed extracts can form transparent, uniform and water-soluble coating layers with good gas and oil barrier properties, and high water vapor permeability. They have been widely used for coating meat products, fruits, and vegetables and also for encapsulating functional ingredients in food products [44].

10.3.1.5 *Pectin*

Pectin, one of the main components of the plant cell wall, is a complex anionic polysaccharide composed of poly α -1,4-galacturonic acids. Citrus peels and apple pomace are the main industrial sources for extracting this polysaccharide. It is widely used as a stabilizing, gelling, or thickening agent in food products [45]. Due to its edibility, biocompatibility, and

selective gas permeability, it has been used for forming films and coating food products such as chicken fillets [46], fish [47], fruits [48], and vegetables [49]. It also has been widely used for encapsulating bioactive agents in food systems [50–52].

10.3.1.6 *Other Polysaccharides*

Other polysaccharides used for coating food commodities include different gums classified in three main groups named as plant exudates (acacia gum [53, 54], gum karaya [55], Persian gum, and tragacanth gum [13]), microbial gums (pullulan [56], xanthan gum [57], and gellan gum [58]), and seed gums (guar gum [59], locust bean gum [60], and basil gum [61]).

10.3.2 **Proteins**

Protein-based coatings are edible since food-grade proteins and additives are used. Hydrophobic interactions, disulfide bonds, and hydrogen bonds are the main interactions occurring while forming protein-based coatings. Any factor affecting these interactions might alter the mechanical and barrier characteristics of the final coating on the food surface [62].

Proteins used for coating food are derived from different plants or animals. Soybean and corn are two of the main sources of plant-based proteins; while casein, whey proteins, collagen, and gelatin are some of the most important animal-origin proteins used for coating the foods [3].

10.3.2.1 *Collagen and Gelatin*

Collagen is the most commercially successful edible protein used for coating food. It is a hydrophilic fibrous protein being the major constituent of connective tissue, skin, and tendon. Collagen-based coatings are mechanically strong, water-insoluble, and good oxygen barriers. However, they are not particularly good moisture barriers.

Collagen has been traditionally used for the production of edible sausage casings, replacing those previously made from natural gut. Collagen has also been recently used for coating fruits [63].

Gelatin protein results from controlled hydrolysis of collagen. Gelatin-based edible coatings are able to reduce the transfer of gas, oil, and moisture from the food surface [3]. Gelatin coatings containing natural antimicrobial agents have been previously used for improving the shelf-life of meat [64–66] and fruits [67, 68]. It has also been used for decreasing fat uptake in deep-fat fried foods [14].

10.3.2.2 Corn Zein

Zein is composed of prolamins which are a group of alcohol-soluble proteins found in corn endosperm. Zein has a hydrophobic nature, which is attributed to its high content of non-polar amino acids. Zein-based coatings are traditionally used for coating fruits, confectionery, nuts, and candies [3]. Recent researches show the use of zein-based coatings for enhancing the shelf-life of melon [69], guava [70], and egg [71], enhancing the survival of probiotic bacteria in gastric fluid [72], and controlling the release of bioactive components [73]. Zein coatings have also been reported to reduce oil uptake in deep-fat fried foods such as mashed potato balls [14]. Antimicrobial zein-based edible coatings incorporated with sorbic acid, calcium propionate, or nisin have been reported to be effective in controlling *Listeria monocytogenes* in cooked sweet corn [74] and ready-to-eat chicken [75].

10.3.2.3 Soy Protein

Soybeans contain much higher protein content in comparison with cereal grains. Most of the proteins in soybeans are water-insoluble [3]. Soy proteins-based coatings have been used for inhibiting lipid oxidation in nuts [76], retaining moisture, delaying lipid oxidation and deterioration in meat products [77–79], reducing fat-uptake in deep-fat fried foods [80], and enhancing the shelf-life of eggs [81] and fruits (such as fresh-cut pineapple [82], fresh-cut apples [83], Persian lime [84], artichoke [85]). It also has been used as a delivery system for bioactive compounds [86].

10.3.2.4 Whey Protein

Whey protein is a major type of milk protein, which remains soluble after precipitation of casein at pH = 4.6. They are heat-labile and globular naturally. The coatings made from this protein have a glossy and transparent appearance with good mechanical characteristics [3]. They are excellent barriers against lipid, oxygen, and aroma. Therefore, they have been widely used for improving the appearance and shelf-life of nuts [87, 88], eggs [89], confectionary [90], meat [91, 92], fruits and vegetables [11, 93, 94]. Whey protein-based coatings have also been widely used as a carrier for bioactive agents such as probiotic bacteria [95], lactoperoxidase, and α -tocopherol [96] for improving the functional properties of different food products.

10.3.2.5 Casein

Casein represents approximately 80% of the total milk proteins. Sodium and potassium caseinates are used in preference to calcium and magnesium caseinate as they are more soluble and have better functional characteristics. Casein molecules, due to their ability to interact together through hydrogen bonds, form compact coatings without needing further treatment. The casein coating layer on the food surface has been reported to be flavorless, transparent, flexible, and water-soluble [3, 97]. The casein edible coatings enriched with essential oils and bacteriocins have been reported to retard microbial contamination in fruits [98]. Casein has also been introduced as a promising agent for encapsulating sensitive food ingredients and bioactives [99, 100].

10.3.3 Lipids

Lipids are usually incorporated into food coatings to impart hydrophobicity and thus reduce moisture transfer. Different types of lipids are used for this purpose. The most commonly used hydrophobic materials in food coatings are waxes. Carnauba wax, beeswax, shellac wax, polyethylene wax, or candelilla wax are the most common waxes in the structure of food coatings [3, 101].

10.3.3.1 Shellac Wax

Shellac is a natural wax secreted by the lac insect. It has been approved by the FDA (Food and Drug Administration) for some foods since 1939. Due to its excellent coating ability and its shiny appearance, it has been used as an edible coating for fruits, vegetables, and confectionery products since the beginning of the 21st century [102, 103]. In recent researches, the combination of shellac wax and other biopolymers such as gelatin has been used for improving the shelf-life of various fruits [104, 105].

10.3.3.2 Carnauba Wax

Carnauba wax is obtained from the leaves of a Brazilian palm tree (*Copernicia cerifera*). Refined carnauba wax is mostly composed of saturated long-chain alcohols and saturated wax acid esters containing 24–32 hydrocarbons. Therefore, it is an excellent barrier to moisture while poor barrier against gases [106]. Carnauba wax has been considered as GRAS and is allowed to be used in the formulation of coatings applied on fruits and vegetables, confectioneries, and chewing gums [107].

The main problems with using carnauba wax as a food coating material are its relatively poor gas barrier and its loss of gloss during storage. To overcome these drawbacks, it can be combined with shellac. Johnfresh™ is a commercial food coating wax composed of both carnauba wax and shellac [1].

10.3.3.3 *Candelilla Wax*

Candelilla wax is an exudate of the candelilla plant which mostly grows in the US and Mexico. It is considered as GRAS and has been used for coating different foods such as hard candy, chewing gum, fruits, and vegetables [108–111].

10.3.3.4 *Beeswax*

Beeswax is secreted by honeybees and is separated from the honey section by centrifuging. It is a complex mixture of hydrocarbons, monofunctional alcohols, and long-chain acids. It is considered a GRAS and that is permitted to be directly used in food with some limitations. The maximum permitted level is 0.005% in confections and frostings, 0.065% in chewing gum, 0.1% in soft candy, 0.04% in hard candy, and 0.002% in all other categories. It has been used in different food coatings for applying on the surface of fruits [2, 112, 113] and also for encapsulating bioactive agents [27].

10.3.4 Additives

The organoleptic, functional, nutritional, and technological characteristics of edible coatings can be modified with the aid of different additives.

Due to the high brittleness of the polymer-based coatings, the most frequently used additives in their structure are plasticizers. Plasticizers are low-molecular-weight components which locate between polymer chains. They decrease intermolecular forces, increase the mobility of the polymer chains, and therefore improve the film flexibility. Common plasticizers used for edible coatings are saccharides (glucose, fructose glucose syrups, and sucrose) and polyols (sorbitol, glycerol, polyethylene glycols, and glyceryl derivatives).

Coating functionality on the food surface depends on the adhesion between the coating and food surface. Surfactants such as Tweens, lecithin, or Spans are surface-active components being able to reduce the surface tension at the water-solid interface contributing to wettability improvement and better adhesion of the coating solution on the food surface.

They are also necessary for the stability of polysaccharide or protein coatings containing hydrophobic substances [3].

Texture enhancers, antibrowning and antimicrobial agents, nutraceuticals, aroma precursors, nutrients, probiotics, colorants, flavors, and nanoparticles are other additives used in the formulation of food coatings [1].

10.4 Application Methods of Edible Coating on Food Surface

For coating a food product, the coating solution should be applied on its surface and the coating form after solvent evaporation. Typical methods used for forming polymer-based edible coatings are dipping, enrobing, panning, and spraying [5]. The three latter methods are commonly used in the food industry; while dipping is usually employed for lab-scale coatings [114].

The dipping is best-suited for products with irregular shapes. In this method, the product is dipped into the coating solution for a specific duration of time and then drains off and dries. This method is simple and cheap and does not require sophisticated machinery equipment. However, the final formed coating might not be uniform enough. Therefore, in some cases, multiple dipping may be necessary to ensure full coverage [62, 115]. Moreover, difficulty in controlling the process, microorganism growth in the dipping tank, dilution of the coating solution, and residual of a high quantity of it at the end of the process are some of the major challenges of this method [114].

The enrobing method is more common for coating food products with flat surfaces in the meat and chocolate industry. During this process, the coating solution flows vertically to the food product. Gravitational and viscous forces are important in the coating process. For controlling the coating thickness on the final product, the viscosity of the coating solution is a key parameter that should be adjusted properly [114, 116].

The panning technique is usually used for coating confectionery products. In this method, the product is placed in a large rotating pan. The coating material is sprayed or poured into the pan. The pan rotates and the coating material evenly distributes over the food surface. Finally, forced air is used to dry the coating [62, 117].

The spraying technique is preferred for coating products with a large surface area. In this method, food is placed on a plate which rotates under a hand-held spraying gun. This process continues until achieving the desired coating thickness. Finally, a uniform coating layer with controlled thickness

is formed over the food surface. However, when using the spray-coating technique, the bottom surface of the food should be coated separately after drying the initial coating layer [62, 115].

10.5 Food Applications of Edible Coatings

10.5.1 Fruits and Vegetables

Fruits and vegetables are living tissues that undergo respiration, transpiration, and ethylene production after harvest, and thus, major physical, chemical, and microbiological changes occur during storage contributing to changes in their appearance, flavor, texture, and nutritional aspects [10].

Coating fruits and vegetables with biopolymer-based coatings can retard the transfer of gas, water vapor, and volatile compounds through their surface and thus provide them with a modified atmosphere which reduces the rate of respiration and senescence, retains moisture, reduces aroma loss, and delays color changes and microbial contamination during storage [13, 33]. Vu, Hollingsworth [118] enhanced the shelf-life of strawberries by coating them with chitosan-based solutions (Figure 10.2).

Edible materials used for coating fruits and vegetables are composed of hydrocolloids, (consisting of either proteins or polysaccharides) or hydrophobic compounds (e.g., waxes). Successful fruit coatings are usually composed of a mixture of hydrocolloids and hydrophobic compounds [1]. Since now, different polysaccharides (e.g., chitosan [31], starch [38], carboxymethyl cellulose [119], gellan [120]), proteins (e.g., soy protein isolate [82], zein [69], gelatin [67], gluten [121], whey protein isolate and calcium caseinate [122]), and waxes (such as carnauba

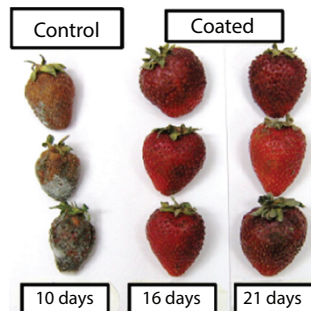


Figure 10.2 Uncoated and coated strawberries with chitosan-based coatings after 10, 16, and 21 days storage at 4°C. The figure has been reproduced with permission from Vu, Hollingsworth [118].

Table 10.1 Applications of polymer-based edible coatings for improving the quality and extending the shelf-life of different fruits and vegetables.

Fruit type	Main polymer	Additives	Results	Reference
Apple	Starch	Glycerol and calcium chloride	Decreased weight loss and improved appearance	[227]
	Chitosan	Stevia extract	Reduced the total yeast and mold contamination	[32]
	Soy-protein	Glycerol and ferulic acid	Controlled weight loss and firmness	[83]
Strawberry	Chitosan and CMC		Maintained volatile aroma and firmness	[228]
Tomato	Alginate and chitosan	<i>Flourensia cernua</i> extract	Inhibited microbial growth and reduced weight loss and gas exchange rate	[229]
	Starch	Sorbitol	Retarded ripening and deterioration rate of tomatoes up to 20 days	[230]
	Pullulan	<i>Laminaria japonica</i> -derived oligosaccharides	Reduce respiratory intensity, vitamin C loss, weight loss and softening, increased titratable acidity, and the overall likeness of fruit	[231]

(Continued)

Table 10.1 Applications of polymer-based edible coatings for improving the quality and extending the shelf-life of different fruits and vegetables. (*Continued*)

Fruit type	Main polymer	Additives	Results	Reference
Banana	Soybean protein isolate	Cinnamaldehyde and zinc oxide	Reduced ripening rate, weight loss, enhanced firmness, titratable acidity, and sensory quality	[232]
	Starch	Sucrose esters	Retarded the senescence, reduced weight loss, and chlorophyll degradation, resulted in a 40% extension in banana shelf-life	[20]

wax [123, 124], beeswax [112], candelilla wax [109], or shellac [125]) have been used for this purpose. Fruit coatings can also be potential carriers of additives that help to preserve or even improve the quality of the product. Antimicrobial compounds (e.g., potassium sorbate) [126], anti-browning agents (e.g., ascorbic acid) [127], nutrients (e.g., vitamin E) [128], texture enhancers (e.g., calcium chloride) [129], probiotics (e.g., *Bifidobacterium lactis*) [130], aroma precursors (e.g., linoleic acid) [131], and flavors and colorants (e.g., apple puree) [132] are different additives incorporated into edible coatings applied on the surface of fruits and vegetables. Table 10.1 shows the components of some of the coatings recently applied on apple, strawberry, tomato, and banana that successfully enhanced their shelf lives. As it is observed, improving appearance, decreasing weight loss, retarding ripening, inhibiting microbial growth, and maintaining the firmness, aroma, and nutritional compounds are the main achievements resulted from coating these fruits and vegetables.

10.5.2 Meat and Meat Products

Meat, due to its high moisture content and the availability of nutritional and functional components on its surface, is susceptible to shrinkage, development of microorganisms (especially *Listeria monocytogenes*), chemical deterioration, enzymatic autolysis, and lipid oxidation which contribute to discoloration and changes in flavor, aroma, and other organoleptic characteristics during processing, handling, and storage [133, 134]. Moreover, in the case of freezing meat for achieving a longer shelf-life, they become susceptible to freeze burn and dehydration during storage. These changes result in substantial economic losses for producers as well as a considerable risk for consumers' health [135, 136]. Edible coatings are able to retard these changes. Volpe, Siano [137] improved the shelf-life of fish fillet with the aid of carrageenan-based coatings (Figure 10.3).

Polymer-based edible coatings act as barriers against the migration of oxygen, moisture and carbon dioxide. They also enable incorporation of functional natural extracts to prolong shelf-life, improve sensory and nutritional quality and retain the market value of meat and its products [138]. Various types of coating formulations have been used for this purpose [135]. They are usually composed of a polymeric basis with different functional additives incorporated into it.

Among the different biopolymers, chitosan is the most commonly used polymer for coating meat, poultry, and seafood. It is used as a polymeric basis as well as antimicrobial and antioxidant agents [139–152]. Other previously used polysaccharides and proteins for coating meat and meat products include carboxymethyl cellulose [133, 153–155], pectin [46, 156], starch [156–158], alginates [155, 156, 159–162], carrageenan [156], tragacanth [163], salep [163], whey protein [91, 134, 164–166], soy protein [77, 167], gelatin [156, 168, 169], sodium caseinate [170], egg albumin [167] and zein [171].



Figure 10.3 Uncoated (left) and coated with carrageenan (right) fish fillets after 7 days of storage at 4°C. The figure has been reproduced with permission from Volpe, Siano [137].

Polysaccharide- and Protein-based coatings, due to their hydrophilic nature, have selective permeability for oxygen and carbon dioxide and resist lipid migration and therefore, are able to extend the shelf-life of meat products by preventing oxidative rancidity, dehydration, shrinkage, and surface browning and improving juiciness and texture of the meat product. However, they usually have insufficient moisture barrier effects and low mechanical resistance, and therefore, might become fragile under mechanical stresses [172].

Lipids are efficient barriers against moisture migration. The main lipids used for coating meat products are natural waxes (such as paraffin wax and beeswax), acetoglycerides, resins, fatty acids, and both vegetable (e.g., sunflower oil [46]) and animal oils (e.g., krill oil [173]). They are either used as separate coatings or incorporated into protein- and polysaccharide-based coatings to make composite coatings [174]. Lipid incorporation can improve hydrophobicity, cohesiveness, and flexibility of the coating. This can help to extend the freshness and the stability of color, aroma and tenderness as well as the microbiological quality of fresh and processed meat products. However, it should be noted that these types of coatings may confer an undesirable taste to meat products [172].

There are also other additives that have been previously incorporated into edible coatings used for meat and meat products. They include organic acids (e.g., gallic [143], malic [164], benzoic, lactic, propionic, acetic and sorbic acids), antioxidants (e.g., tea polyphenols and vitamin C [160], bamboo vinegar [152]) polypeptides, fatty acid esters, and bacteriocins (e.g., lactoperoxidase [175], lauric arginate ester [144], peroxidase, lysozyme [165, 166], nisin [140, 144, 159, 161, 164], sodium lactate [156] and sodium diacetate [139]); plant essential oils (e.g., essential oils extracted from oregano [134, 151, 162], rosemary [154, 159], clove [134, 147], ginger [170], *Satureja khuzestanica* [150], *Thymus vulgaris* [176], *Satureja thymbra* [153], *Origanum virens* [91], *Ziziphora clinopodioides* [133, 155], *Mentha spicata* [133], *Zataria multiflora* [142, 149], cinnamon [46, 159, 161], nettle [177], garlic [46] and lemongrass); plant extracts (e.g., sour lemon peel extract [157], grape seed extract [145, 164], apple peel extract [155]), flavoring and coloring agents (e.g., curcumin [46], pomegranate juice [142]), nanoparticles (e.g., zinc oxide nanoparticle [155]) and probiotic bacteria are the most common.

Table 10.2 shows some of the recent researches carried out on coating meat and meat products. As it is observed, retarding moisture loss, inhibiting microbial growth and lipid oxidation, maintaining the color during storage and thus improving the shelf-life are the main achievements resulted from coating meat and meat products.

Table 10.2 Applications of polymer-based edible coatings for improving the quality and extending the shelf-life of meat and different meat products.

Product	Coating polymer	Additives	Results	Reference
Chicken fillets	Whey Protein Isolate	Oregano or clove essential oils	Inhibited microbial contamination and enhanced the storage time from 6 to 13 days	[134]
	CMC	<i>Ziziphora clinopodioides</i> and <i>Mentha spicata</i> essential oils	Reduced the number of test pathogens and increased the shelf-life	[133]
	Chitosan	Pomegranate juice and <i>Zataria multiflora</i> essential oil	Decreased total viable counts of microorganisms, decreased peroxide value, Thiobarbituric acid reactive substance values and protein oxidation, improved sensory scores	[142]
Pork	Chitosan	Gallic acid	Inhibited lipid oxidation and myoglobin oxidation	[143]
	Chitosan	Nisin + gallic acid	Inhibited microbial growth, decreased protein and lipid oxidation, helped to maintain color	[140]
Beef	Chitosan	<i>Zataria multiflora</i> essential oil and sumac extract	Inhibited lipid oxidation and microbial growth	[149]

(Continued)

Table 10.2 Applications of polymer-based edible coatings for improving the quality and extending the shelf-life of meat and different meat products. (*Continued*)

Product	Coating polymer	Additives	Results	Reference
Fish	CMC	<i>Satureja thymbra</i> EO	Controlled oxidative deterioration, extended the shelf-life up to 35%	[153]
	Sodium alginate	Vitamin C and tea polyphenols	Retarded the decay and water loss, reduced chemical spoilage and increased the overall sensory quality	[160]
Turkey Frankfurter	Whey protein isolate	Grape seed extract, nisin, malic acid, and ethylenediamine tetraacetic acid	Inhibited microbial growth	[164]
Cooked pork sausages	Chitosan	Clove essential oil	Retarded microbial growth and sensory changes and significantly enhanced shelf-life	[147]
Cold-smoked fish	Whey protein isolate	Lysozyme	Retarded microbial growth	[165, 166]
Cooked pork chops	Chitosan	Bamboo vinegar	Retarded lipid oxidation maintained the color and improved shelf-life	[152]
Portuguese sausages	Whey protein concentrate	<i>Origanum virens</i> Essential oils	Inhibited the total microbial load, prevented lipid oxidation and color fading, extended the shelf-life	[91]

10.5.3 Bakery Products

The main aims of coating bakery products are to prevent microbial growth and to slow down moisture migration across their surface and thus to maintain their quality during storage [3]. Edible coatings can prevent moisture absorption in bakery products with low moisture content such as biscuits and crackers and also reduce the rate of moisture loss in bakery products with higher moisture content such as bread and cake.

Bartkiene, Bartkevics [178] improved the shelf-life of wheat bread by coating it with a starch-based coating containing lactobacilli and cranberry extract as natural antifungal agents. Saraiva, Naponucena [179] coated cake with starch-based coatings incorporated with citric acid and potassium sorbate as antimicrobial agents. They reported that coating maintained the quality parameters including their moisture, hardness, and elasticity and inhibited the growth of yeasts and molds during storage.

10.5.4 Cheese

During the storage of cheese, contamination by microorganisms and moisture loss may increase the hardness of the final product and undesired organoleptic properties [180]. Coatings can act as a barrier against carbon dioxide, oxygen, and moisture loss preventing dehydration of cheese during the storage and controlling the maturation rate. They can also act as carriers of flavoring, nutritional agents, antimicrobial components (e.g., nisin, natamycin, lysozyme, essential oils, and organic acids), colorants, or sweetener agents [181, 182].

Proteins (e.g., zein [183] and whey protein [184]) and polysaccharides (e.g., chitosan [181, 185], alginate [186] and agar [187]) have been widely used for coating cheese. Water solubility is the main advantage of these types of polymers. Only a few studies showed the potential use of waxes for coating cheese. Previous researches show that beeswax is the one already applied to the cheese with success. It has been reported that hot-melting methods or organic solvents should be used during applying wax-based coatings to cheese and this has limited their application for cheese coating [182].

10.5.5 Nuts

Nuts are a generic term for almonds, peanuts, walnuts, pistachio, ginkgo nuts, pine nuts, etc. [76]. They usually add a desirable crunch and a specific flavor to many foods or might be consumed individually as snacks.

Nuts are rich in polyunsaturated fatty acids which can decrease the risk of stroke and cardiovascular disease in humans. However, due to the high content of polyunsaturated lipids, they are susceptible to lipid oxidation and the formation of off-flavors (oxidative rancidity) [188]. The other most common forms of spoilage of nuts are lipid migration in food systems, fungal growth, and absorption of foreign odors and moisture contributing to texture changes and loss quality [3].

Edible coatings with hydrophobic character can prevent moisture absorption of nuts and help to maintain their crispiness during the storage. On the other hand, coatings with hydrophilic character can act as oxygen barriers which limit oil oxidation and fungal growth and also resist against lipid migration from nut surface. Chitosan [28, 189–191], cassava starch [192], sodium alginate [193], whey protein isolate [88, 188, 194], and soy protein isolate [76, 192] have been recently used for this purpose. They might also contain antioxidant (e.g., *Laurus nobilis*) and antimicrobial agents to enhance the shelf-life of nuts [191]. However, coating nuts, which have hydrophobic surfaces, with hydrophilic coatings is quite difficult due to the differences in the chemical nature of the two compounds. During this process, the dewetting of the coating solution by the nut surface occurs which results in cracking and shrinking of the coating material during drying. Previous researches have shown that increasing the roughness of the nuts surface and addition of surfactants to the coating solution are effective in facilitating the wettability and coverage of nuts with the coating materials [188].

10.5.6 Eggs

Fresh eggs are excellent protein sources. Nevertheless, they are highly perishable and can lose their carbon dioxide and moisture through microscopic pores in their shell contributing to weight loss, interior quality deterioration, and major economic losses. In addition, different microorganisms penetrate through the pores and contaminate the internal content [195].

Edible coatings can maintain egg quality by preventing microorganism, moisture, and gas migration through the eggshell and enhancing shell strength [115]. Coatings based on either polysaccharides (e.g., chitosan [196–198], CMC [199], MC, and HPMC [200]), proteins (e.g., whey protein [71, 89, 201], zein [71], soy protein and wheat gluten [199]), or waxes (e.g., Shellac [202]) have been used for this purpose. However, it has been reported that among the different types of coatings, polysaccharide-based coatings are preferred for coating eggshells due to

their greater transparency, lower thickness, and higher flexibility [115]. Hydrophobic additives could be added to decrease the moisture loss and enhance the wettability of the coating solution on the egg surface. Suppakul, Jutakorn [200] used MC and HPMC-based coatings containing polyethylene glycol, stearic acid, and palmitic acid for improving the shelf-life of eggs. Wardy, Torrico [203] preserved the internal quality of eggs using chitosan-soybean oil emulsions.

10.5.7 Fried Food

In recent years, there has been an increasing demand for consumption of fried food. However, after frying, these products may absorb a large amount of fat which contributes to the high risk of cardiovascular diseases, obesity, and certain cancers [204].

During the frying process, in the first 60 s, moisture molecules rapidly evaporate from the surface of the product. Then, the water migrates from the center of the food to its surface. This results in forming empty voids on the food surface that can be easily filled with fat molecules contributing to an oil concentrated crust (Figure 10.4) [205].

Edible coatings make compact and protective layers on the food surface with fewer pores, which prevent the migration of moisture molecules from the surface of the food. Therefore, the moisture molecules on the food surface cannot be replaced by the oil [206]. If the coating material has gelling abilities, during heating, a thermo-reversible gel forms around the food, which captures water and stops the migration of water out and oil inside the product contributing to a moist, tender, and soft core with a uniform

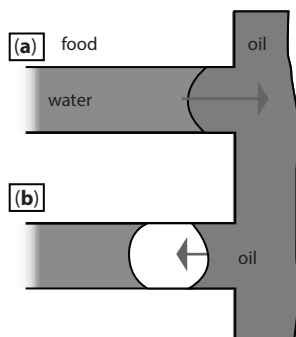


Figure 10.4 Water migration from the center of the food to its surface (a) and fat migration to the food crust (b). The figure has been reproduced with permission from Mellema [226].

crispy crust [207]. Besides, coatings can decrease the oil absorption of the food surface by decreasing the surface hydrophobicity. Therefore, it is preferred to choose a hydrophilic coating material such as proteins (e.g., gelatin, egg white, sodium caseinate, wheat gluten, soy protein, and whey protein) or polysaccharides (corn starch, cellulose derivate, carrageenan, gums, and pectin) for this purpose. It has been mentioned that coatings with high viscosity (such as gums) are much easily applicable to the food surface in comparison with those with low viscosities (such as proteins). These coatings can either act as a lipid barrier after forming thin films around the food or by their gelation properties during frying. Moreover, functional components can be added to the coating materials which can improve the nutritional value of the fried food and also control the transfer of fat and moisture across the surface of fried food [207].

Fry Shield™-calcium pectinate is one of the commercially available coatings used for reducing oil uptake of food products such as frying potatoes, fish, and vegetables. The spraying and dipping techniques are usually used for this purpose [207].

10.6 Microencapsulation of Bioactive Components in Food Systems

Bioactive components in food including proteins (e.g., enzymes or peptides), lipids (e.g., conjugated linoleic acid, fat-soluble vitamins, and omega-3 fatty acids), minerals (e.g., Fe, Se, and Zn), or live cells (e.g., probiotics) play significant roles in our well-being. There are also various molecules that determine organoleptic properties of food such as flavor and color. Most of these components cannot be incorporated directly into the food systems due to their sensitivity to processes or incompatibility with other ingredients. For example, probiotic cells, as functional food components, usually lose their viability and benefits during common food processes. Fat-soluble vitamins such as vitamin A or D are other examples of bioactive components that require encapsulation. They cannot be directly added to a water-based formulated juice due to the phase separation of immiscible liquids.

Microencapsulation is defined as a process in which a semipermeable polymeric membrane or matrix encloses sensitive materials leading to the formation of special microparticles or microcapsules that can release their content in a particular location under a controlled manner [208, 209]. This process is introduced as an approach to meet the nutritional or technological challenges in the production of formulated foods.

The main objectives of encapsulating bioactive components in food systems include:

- Protecting sensitive materials against evaporation, unwanted chemical interactions, and immigration of some molecules in food;
- Improving stability and activity of bioactive components during food processing, storage, and consumption;
- Masking off-flavors;
- Facilitating the handling and utilization of food ingredients;
- Delivering active component to their target site in the body, e.g., mouth, stomach, and colon, and releasing them controllably.

On the other hand, microencapsulation leads to an increase in complexity and cost of food chain production. In addition, microcapsules may have undesirable impacts on the food appearance and texture leading to a negative effect on its marketability. Although this process has not been prevalently used by food producers, current demands for tastier and healthier foods made microencapsulation an interesting topic to academics and industry owners.

10.6.1 Terminology

Key terms of microencapsulation and delivery systems for food systems include:

Delivery system: All mechanisms and processes engaged with microencapsulation, delivery, and release of active components [210].

Active component: A sensitive food component that is encapsulated in a polymeric microparticle or microcapsule. This component could be a bioactive molecule, live cell, or volatile compound. Molecular characteristics (e.g., molecular weight, spatial structure, density, charge, polarity, and physical state) and sensitivity of active component to ambient condition determine the type of wall materials and the technique being used for microencapsulation. The active component is also called “active agent”, “fill”, “core material”, “internal phase”, or “payload phase” [210, 211].

Wall material: A single or a combination of food-grade components including polysaccharides, proteins, fats, or surfactants that enclose active component. Wall material is also called “carrier material”, “shell”, “matrix”, “membrane”, “encapsulant”, or “external phase” in different sources. Wall material may have a homogenous or heterogeneous structure depending on its constituents and fabrication method [210, 211].

Delivery process: The process of carrying an encapsulated active component into a specific site in the body like mouth, nose, stomach, small, or large intestine.

Controlled release: The process of releasing active components in the proximity of their target site with a specific concentration-time profile. Common terms used in the context of controlled release are:

- **Targeted release:** Release of the active component in a specific location within the body such as mouth, stomach, or colon;
- **Triggered release:** Release of active component in response to specific mechanical stress like chewing or environmental stimulators like alternation in pH, ionic strength, temperature, or enzymatic activity;
- **Burst release:** Releasing a major part of active components over a short period;
- **Sustained-release:** Gradual release of active components during a long period under a relatively constant rate [210].

10.6.2 Structure of Microcapsules

The structure of microcapsules can be classified into two main groups including mono-core and poly-core structures (Figure 10.5). In the mono-core structure, the active component is usually coated by a single- or multi-layer wall. However, in the poly-core structure, several active components are confined in a matrix or polymeric network within a single microparticle. The poly-core structure is more resistant to mechanical stresses than the mono-core type. However, the active component may be located on the surface of the particle and get exposed to the surrounding environment. In the poly-core structure, the active component distributes in the

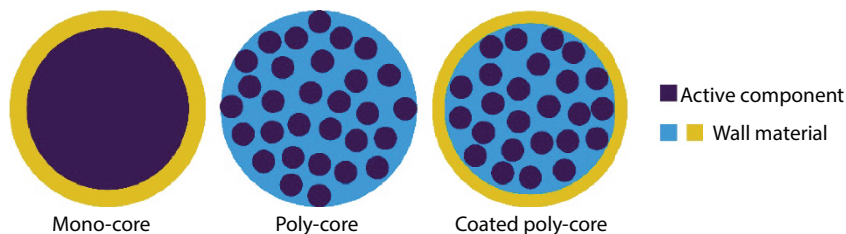


Figure 10.5 Different structures of microcapsules.

wall material network in the form of small emulsion droplets, live cells, and discrete or aggregated active molecules. A combination of these two structures leads to a coated poly-core structure, which has benefits of both.

10.6.3 Materials for Microencapsulation

The wall material or matrix should be able to protect the active component against chemical, physical, or biological destructions. Besides they should prevent the release of the active component before arriving at their target site. Numerous synthetic and natural polymers are prevalently used for medical and pharmaceutical purposes in delivery systems. However, wall materials for food applications should be GRAS and prevent releasing active component during processing, transportation, and storage of food. Thus, many studies are currently being carried out by researchers to use various food-grade biopolymers in targeted delivery systems. Among all, proteins and polysaccharides are the most common biopolymers because they are biocompatible, biodegradable, and able to release their content controllably in the presence of environmental stimulators [212, 213]. In the food industry, biopolymers have been used as fat-replacers in low-calorie products for many years, because they resemble organoleptic and textural characteristics of fat droplets in food matrices. Recently, their applications in microencapsulation and targeted delivery systems have attracted much attention from food researchers.

The most diverse biopolymers being used as wall material for microencapsulation of bioactive compounds and live cells in food systems are polysaccharides. Starch and its derivatives (e.g., amylose, amylopectin, dextrins, maltodextrins, and polydextrose), cellulose and its derivatives (e.g., CMC and HPC), plant exudates (e.g., galactomannans, pectins, tragacanth gum, and soluble soybean polysaccharides), seaweed gums (e.g., alginates and carrageenans), and animal or microbial polysaccharides (e.g., chitosan, xanthan, and dextran) have been used for microencapsulation in food systems. Proteins are also employed for microencapsulation in food systems. Whey protein concentrate, whey protein isolate, egg albumin, collagen, gelatin, zein, and casein have been widely studied as proteinous wall materials. Acacia gum, which is a complex of glycoproteins and polysaccharides, has been also used for microencapsulation of food flavors and live cells in food systems [214]. Lipids such as fatty acids, fatty alcohols, waxes (e.g., beeswax or carnauba wax), glycerides, and phospholipids are also suitable for microencapsulation of lipophilic active components in food.

10.6.4 Microencapsulation Techniques

One of the most crucial steps in preparing an efficient delivery system is the microencapsulation process, which should be chosen and performed regarding functional properties and molecular characteristics of the active component and wall material. Up to now, various strategies have been used to microencapsulate bioactive materials for food applications, including aerosol-assisted techniques (e.g., spray-drying, spray-cooling, and electro-spraying), freeze-drying, emulsification techniques, and extrusion. In this section, a brief overview of the most common microencapsulation techniques is presented.

10.6.4.1 *Spray Drying*

Spray drying is the oldest microencapsulation technique in the food industry so that 80%–90% of food products containing encapsulated components are currently prepared by this method [208]. In this technique, the active component is thoroughly blended with the wall material, sprayed into a chamber, and exposed to hot airflow leading to sudden evaporation of the solvent. Then, the dried microparticles containing the active component are collected in a cyclone [215]. Spray-drying has many advantages over other techniques. It is a low-cost, flexible, simple, and continuous process and is able to fabricate microparticles with lower than 40 μm diameter. However, the application of high temperatures in the spray-drying method may damage sensitive components [216]. Moreover, the internal condition of the drying chamber is not uniform and also controlling the size of microparticles is relatively difficult. It should be noted that some researchers believe spray-drying is actually a technique of material immobilization, not an encapsulation method. Because, not only some active component may locate on the surface of microparticles and get exposed to the surrounding, but also they may release instantly in an environment which contains their solvent [208, 215].

10.6.4.2 *Spray Cooling*

Spray-cooling or spray-chilling is basically similar to the spray-drying in which a mixture of the active component and wall material is sprayed into a closed chamber. However, in this technique, a very cold airflow inside the chamber solidifies droplets into microparticles. Spray-cooling, as one of the cheapest encapsulation methods, is usually employed for lipid matrices.

Some disadvantages of this method are the low encapsulation efficiency of core material in microparticles and gradual expulsion of active component from the matrix (due to crystalline structure and polymorphic rearrangement of lipids) [216]. Lipids with high melting points are often used as wall material in this method. Spray-cooling has been previously used for microencapsulation of enzymes, flavors, minerals, proteins, and probiotics [215, 217].

10.6.4.3 *Freeze-Drying*

Freeze-drying has been used to produce probiotic powders for many years. However, its application for microencapsulation of active materials is relatively new in food products [216]. In this process, active component and wall material are dispersed in water, frozen at -40°C to -90°C and dried under vacuum through the phase transition of ice to vapor. The final product is obtained in the form of a highly porous brittle cake, which may be ground into microparticles by mechanical milling [211]. Since the drying process is carried out at a very low temperature, the functional properties of the active component are preserved better than the spray-drying method. However, formation and growth of ice crystals in the freezing step may injure some active components such as live cells and osmotic stress during drying may lead to loss of viable cells. To diminish the deleterious effects of the freezing step, cryoprotectant compounds such as sugars, polyols, amino acids, carbohydrate polymers, and proteins may be added to the initial mixture. Cryoprotectants are usually accumulated inside cells and modulate osmotic pressure on both sides of the cell membrane [216]. The main disadvantages of the freezing-drying technique are high energy consumption and long processing time. The final product usually has a very porous structure. Therefore, the protective effect of the matrix sharply decreases if the long-term release of the active component is required [208].

10.6.4.4 *Emulsification*

Emulsification is the process of dispersing a fluid into an incompatible or immiscible second fluid. It can be used to produce microcapsules by adding the active component into the first fluid [215]. In this method, the dispersed phase (a mixture of wall material and active component) is added to a high volume of the continuous phase (usually an edible oil) and is homogenized to form a water-in-oil emulsion. Upon the formation of emulsion, the water-soluble wall material becomes insoluble through the formation of crosslinks. Consequently, solid microcapsules are formed in the continuous phase that

is separated by filtration. The size of microcapsules is usually adjusted by controlling homogenization speed, which can produce particles with 25 μm to 2 mm diameter [216, 218]. Usually, by increasing the homogenization speed, the encapsulation efficiency of the active component decreases to some extent. Smaller particles can be formed by adding emulsifiers to reduce the interfacial tension of the two phases. Emulsification can be easily used for scale-up production of microcapsules. However, the complexity of the process and impossibility of continuous production have put some limitations on its application. Since expensive edible oils such as soybean, sunflower, rapeseed, or corn oils are used as a continuous phase for food applications, the cost of the process is high. Moreover, the residue of oil in the microcapsules limits the application of this method for low-calorie foods [219, 220].

10.6.4.5 *Extrusion*

Extrusion is the most widely used method for particle formation by hydrocolloids. In this method, the active component is mixed with a hydrocolloid solution, which is actually the wall material. The mixture is slowly pumped into a narrow nozzle that forms pendant droplets at the lower end of the nozzle. These droplets fall into a hardening bath one by one and instantly form spherical particles. Hardening bath may only contain ice water for lipid coatings. However, it often contains multivalent ions (e.g., Ca^{2+} and Mg^{2+}) or enzymes (e.g., transglutaminase) that crosslink polymer chains and make hydrogel networks. The shape and size of the particles depend on the inner diameter of the nozzle, surface tension of the hydrocolloid solution, and distance between the nozzle and the hardening bath [220]. In contrast to spray-drying or spray-cooling, there is more control over droplet formation in the extrusion technique. In addition, uniform particles can be formed by vibrating the nozzle. Moreover, by using a coaxial needle (Figure 10.6) as the extrusion nozzle, it is possible to produce multi-layer particles with heterogeneous structures like coated poly-core structure in a single-stage process. These nozzles provide an opportunity to use incompatible materials without direct contact with each other in the structure of a particle; for example, encapsulation of live cells in wall material containing organic solvents [216].

Extrusion is a simple and low-cost method. Additionally, the gentle formation of particles guarantees high efficiency of active component encapsulation. The main disadvantages of this method are the large-size (2–5 mm) and the slow-rate of particle formation, which makes it difficult to increase the scale of production [220]. Some modifications including the application of multi-nozzle systems, rotating disc atomizers, and cutting jet technique have been performed to increase particle production. Among all, jet-cutter

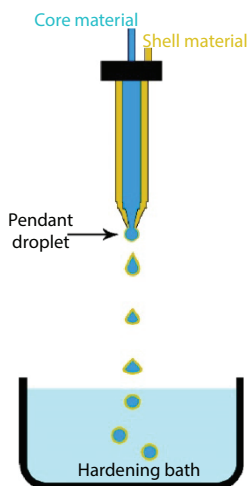


Figure 10.6 Extrusion process using a coaxial nozzle.

technology has the most potential to produce microparticles on the industrial scale [208]. The extrusion method can be carried out under aerobic or anaerobic conditions. The latter is a major advantage for the encapsulation of obligatory anaerobic microorganisms or materials sensitive to oxidation. In this case, the extrusion apparatus is placed in a sterile isolated chamber and oxygen in the chamber is replaced with nitrogen. Up to now, extrusion has been used for microencapsulation of aromas, enzymes, proteins, and living cells.

10.6.4.6 *Electro-Hydrodynamic Atomization*

Electro-hydrodynamic atomization or electrospray is a simple technique conceptually in which a conductive polymeric solution is sprayed into micro- or nano-droplets by strong electrical forces. First, the polymeric solution containing the active component is pumped into a narrow tube, which is connected to a charged electrode. As a pendant droplet is formed, electrical repulsions start competing with viscoelastic force and surface tension of the solution. This leads to the formation of the Taylor cone structure (Figure 10.7). Once electrical forces dominate, the solution is atomized into ultra-small charged droplets. These droplets are forcibly pulled toward a collector, which is connected to the opposite electrode. The collector can be a solid surface or a liquid bath. In the first case, dry microparticles are formed instantly, which is called dry-electrospray; while in the latter case, hydrogel microparticles are usually obtained through the wet-electrospray process (Figure 10.7) [214, 221]. Focusing and controlling

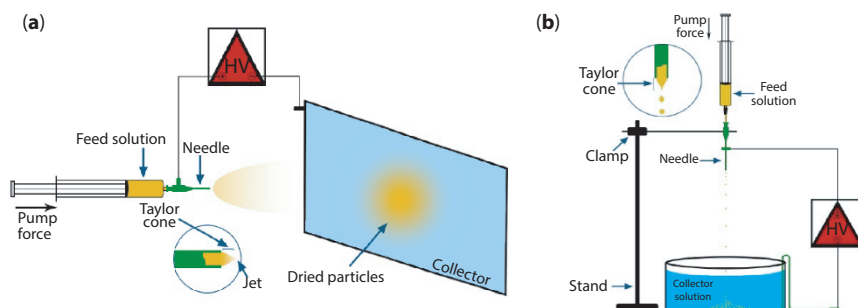


Figure 10.7 Experimental setup for electro-hydrodynamic atomization. Dry-electrospray in horizontal setup (a) and wet-electrospray in vertical setup (b).

the motion of flying charged droplets by external electric fields are easier than uncharged droplets formed by conventional spray systems such as spray drier. Moreover, microparticles produced by electrospray are almost uniform and their deposition efficiency is higher than uncharged ones. Since the process is usually carried out in the ambient condition, it does not involve high temperature, which makes it a suitable choice for micro-encapsulation of heat-sensitive active components such as live cells and antioxidants [222]. Charged microparticles are adequately scattered while flying toward the collector due to electrical repulsions, which prevents agglomeration of the resultant microparticles [223]. Also, it is not necessary to make emulsion before electrospraying and micro-droplets can be formed from fairly viscose solutions [224].

Low productivity of electro-hydrodynamic atomization and blocking the feeding needle are considered as two important drawbacks of the method. The scale of the production can be increased considerably by making some modifications in the injection device, for example, application of porous cylindrical injection devices, multi-nozzle sprayers, or multiple spikes needleless systems. Moreover, blocking the feeding nozzle can be prevented by using needleless systems [225]. Totally, electro-hydrodynamic atomization has a flexible experimental setup, which can be simply modified based on the users' demand.

10.7 Conclusions

In this chapter, coating and microencapsulation of food components were introduced as effective approaches for the production of healthier foods with a longer shelf-life and better organoleptic properties. A successful coating or microencapsulation process strongly depends on the materials

being used for covering the food object. However, the technique used for this purpose plays a significant role. Thus, more studies are required to be carried out for finding new functional edible biopolymers or combination of biopolymers for coating or microencapsulation of food components. Moreover, some innovations are demanded to improve the efficiency of coating/microencapsulation techniques to reduce the cost of process and productivity.

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Biopolymers as Edible Coating for Food: Recent Trends

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Abstract

Edible coating, a primary packaging layer that consists of biopolymers and can be consumed along with the foods, is an all time in demand. Polysaccharides, proteins, and lipids are the major edible biopolymers used in edible coating. The primary function of edible coating is controlling gas and water permeations in food surfaces with its environment. The secondary function includes preventing the products from microbial spoilage and mechanical damage. In addition, the edible coating improves consumer acceptance through enriched organoleptic and sensory attributes of the coated foods. The application of edible coating includes coating of whole and fresh-cut fruits and vegetables, seafood, meat, and its recent application in bakery products. Edible coating is also an active preservation technique for fresh and processed foods with shelf life extension by inhibiting nutritional losses and quality deterioration. These biopolymers act as the carrier material for antioxidant, antimicrobial, and antiviral agents to enhance safety of the food products. Edible coatings are the promising solution to post-harvest losses of perishables, food insecurity, and increasing environmental concerns.

Keywords: Biopolymers, edible coating, food, polysaccharides, proteins, lipids

11.1 Introduction

Biopolymer is the chain of monomer residues derived from biological systems such as plants and animals. These polymers consist of repeating units

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of sugars or amino acids or aliphatic polyesters from the biological sources. Polysaccharides and proteins are the two major biopolymers used in food industries. The interaction of biopolymers with food molecules assists in freezing, texture modification, gel and network formation that aids in developing edible films and coatings [1].

Biopolymers are also known as green polymers that have potential to degrade itself without any further processes or foreign agents. Most of the biopolymers are hydrocolloids, which possess various functional properties including formation of intermolecular interactions between the compounds that resulted into a film matrix and coating network. Biopolymers possess the potential to form coatings and films that extends the shelf life of fresh and processed foods [2]. Network forming ability, nutritious composition, ability to hold antioxidant and antimicrobial agents, renewable origin, low cost, ready availability, and no negative impact on the environment are the reasons for biopolymers in edible coating. Biopolymers are called as IV generation of packaging [3].

Edible coating consists of biopolymers that are edible and coated directly on the food surface either by immersion of foods into biopolymer solution or by spraying the biopolymer solution over the food surface. It is a primary packaging material for most of the perishable and semi-perishable foods. Edibility and biodegradability are the two major advantages of edible coating. Other advantages include improved aesthetic appearance and enhanced sensory characteristics which lead to high consumer acceptance rates of edible-coated foods.

The promising features of edible coating/films over synthetic as stated by Robertson [4] are as follows:

- It prevents waste occurrence by consuming the packaging material together with food.
- Even if they are not consumed, still will not possess any harm to the nature.
- It can be produced from various agricultural and food industries as a source of byproduct utilization.
- It can enhance the sensory characteristics of the coated product by incorporating flavors, colors, sweeteners, etc.
- It can enhance the nutritional value of the product.
- It prevents migration between other compounds in heterogeneous foods such as pizza, pies, and sweets.
- It carries active agents—antimicrobial and antioxidant.

11.2 Need for Edible Coatings

Food packaging plays the major role in food preservation throughout the distribution chain. The packaging process must balance the food protection and energy utilized for the packaging material production and disposal. The non-degradable nature of plastic packaging materials possesses severe challenges to the increasing landfills and municipal solid wastes. The increasing environmental concerns resulted in implementing strict regulations, which directly reduces production of such polymers [5].

Edible coating replaces the usage of synthetic plastics in the food packaging application. Edible coatings are generally prepared from non-toxic, non-polluting, and low-cost biopolymers that are derived from various agricultural commodities and by-products of food and agriculture processing industries [6]. In economic and ecological perspective, edible coating utilizes the composite biopolymers obtained from cake, meal, flour and straw—the agroindustry by-products [7].

Post-harvest losses are one of the greatest challenges for the fruit and vegetable producers. To overcome these losses, conventional treatments including chemical waxes and fungicides are practiced. However, continuous exposure to these chemicals causes hazardous to health and environment. The increasing consumer awareness among recommended consumption rate of fruits and vegetables and to eliminate the excessive packaging waste generation and landfill [8] paves the way for minimally processing/preserving methods such as edible coating. In edible-coated fruits and vegetables, the physiological changes and microbial growth that causes biochemical changes and quality loss are retarded. Highly perishable fruits are the most appropriate for edible coating, because of their liable nutrient content and short shelf life [9].

The addition of antimicrobial and antioxidant agents in food matrix has been employed to prevent food contamination. However, direct application of these agents leads to neutralized or evaporated or reduced effective concentration on the food surface due to rapid and unstable release mechanisms [10]. To overcome these drawbacks, edible coating has the potential to carry and release the active agents into food in a controlled manner [11].

The presence of antioxidants such as vitamin, polyphenol, etc., in fresh-cut fruits and vegetables having links with the prevention of cancer and degenerative diseases, that increases consumer demand. The major drawback associated with the products of fresh-cut fruits and vegetables are its processing, which causes quality deterioration associated with

tissue breakdown that results in metabolic, physicochemical, and textural changes [12]. Edible coating that carries antioxidant and anti-browning agents is the promising method to preserve fresh-cut produces without any nutritional loss.

Dough freezing, a practice in bakery industries, has been followed for economic advantages [13]. Ice crystal formed during freezing reduced the dough strength and CO₂ retention, prolonged fermentation, reduction in viability, and yeast activity. That reduces the volume and texture of the bakery product [14]. Edible coating provides the necessary gas barrier to the carbon dioxide release from dough, prevents ice crystal formation during freezing, and helps to maintain structure and quality of the final product [15].

11.3 Functions of Edible Coating

The primary functions of edible coating are preventing gas (carbon dioxide, oxygen, and volatiles) transfer and creating a modified atmosphere. Such atmosphere delays fruits and vegetables ripening and extends shelf life. Controlling the oxygen intake leading to retardation of lipid oxidation in meat and also depleted oxygen levels affects aerobic microorganisms and reduces the number of spoilage microorganisms present in the meat and its products [16]. Similar to meat, spoilage of cheese is due to fat oxidation and microorganisms' growth that resulted unacceptable flavor, odor, and appearance changes. These changes can be controlled by applying a low oxygen permeability packaging to avoid oxidation of fats and growth of undesirable microorganisms, which cause modifications in flavor, odor, and appearance [17]. Even in the case of moisture retention in the meat products, biopolymers have turned out as an effective alternative [16].

Softening of fruit and vegetable tissues influences the sensory score and affects consumer acceptance. Softening causes cell wall damage that composed of cellulose, hemicellulose, and pectin. The enzymes, which are responsible for this softening, were pectinmethylesterase (PME) and polygalacturanase (PG). Texture enhancers are added to edible coatings to minimize tissue damages during fruits and vegetables storage [18].

In addition, edible coating acts as an active carrier of preservatives including antioxidants, antimicrobials, and anti-browning agents. Natural sources of these agents are spices, organic acids, fatty acid esters, and essential oils, that can be directly incorporated into the biopolymer solutions [19]. Essential oils have high antioxidant and antimicrobial activities. The efficacies of these essential oils are based on the inactivating mechanism

such as degrading cell membrane, inhibiting enzyme activity, influencing bacterial genetics [20].

Changes in color or browning during post-harvest operations are due to enzyme-catalyzed reactions. Polyphenol oxidase (PPO) is the major browning enzyme that is breaking the phenolic and polyphenolic compounds and reducing the antioxidant activity of fruits [21]. Ascorbic acid, oxalic acid, citric acid, phenolic acid, and resorcinol are some of the anti-browning agents that are used in edible coating [18, 22]. Extending shelf life by employing these agents, hence, edible coating can be considered as one of the food preservation methods.

Edible coating exhibits a diverse function, i.e., edible coatings reduces the oil uptake during frying process, the oils in the fried foods had direct role in diabetic and coronary diseases [23]. The hydrocolloid coating reduces the oil content in the fried foods due to its fat-barrier properties [24].

11.4 Materials Used for Making Edible Coating

The biopolymers used for edible coating are divided based on their origin—plant and animal sources. This can be justified by the fact that a particular coating can only sustain until it is suitable for a specific food commodity.

11.4.1 Plant Source

11.4.1.1 *Starch*

Starch is the most employed agricultural raw material for edible coatings. Plants such as corn, potato, wheat, oat, barley, and soybean are some of the major sources of starch [25]. Such sources determine the physical and chemical status of the starch granules [26]. Starch, a polymeric carbohydrate, consists of two polysaccharides—amylose and amylopectin. Amylose is a linear polymer chain with α -1,4 anhydroglucose units and it is responsible for the cross-linking nature of starches [27]. Amylopectin is a branched chain with short α -1,4 units binded through α -1,6 glycosidic bonding [28].

Starches are generally semi-crystalline in the range of 15%–45% crystallinity. The differences in structure and molecular weight of these two polysaccharides cause variation in coating network formation. The insoluble nature of starch molecules in cold water is because of hydrogen bonding. While heating, crystalline structure disrupts and water interacts with

hydroxyl groups of starch granules. Therefore, formation of amorphous region forms and assists the coating network formation [29].

Garcia, Martino [9] studied the effect of medium amylose—corn and potato starches (250 g/kg starch) and high amylose—amylomaize VI (modified) starch (650 g/kg) on the strawberry coating. The results suggested the high amylose coating forms the better network than medium amylose coating, with reduced weight loss, retained firmness, and extended maturation period. Above all, the shelf life of strawberries increased to 28 days (coated) from 14 days (control).

Chickpea is a legume that contains starch high in amylose having the network-forming ability. The chickpea starch-coated fresh-cut papaya showed negligible weight loss, i.e., 53.65% to 51% in day 12 of storage. Moreover, the water loss barrier created by the coating caused reduction in transpiration. In addition, shelf life is extended to 12 days in coated fruit, whereas the uncoated fruit is spoiled at the 8th day [30].

Figure 11.1 shows the scanning micrograph of uncoated and coated banana peel. The rice starch-coated banana shows uniform surface without any cracks or cleavage on the epidermal cells thus slows down the ripening process. Uncoated banana shows the presence of cleavage and non-uniform surface that indicates the accelerated mass transfer through banana surfaces caused higher respiration rate with other biochemical changes [31]. Similar results were observed for the plum fruit with the same formulation. Here, a significant reduction in respiration rate at the 3rd week of coated plum was observed compared to control samples during storage, which indicates the marketability of uncoated fruit ended by the second week, whereas the coated fruit exhibited extended shelf life for 7 more days [32].

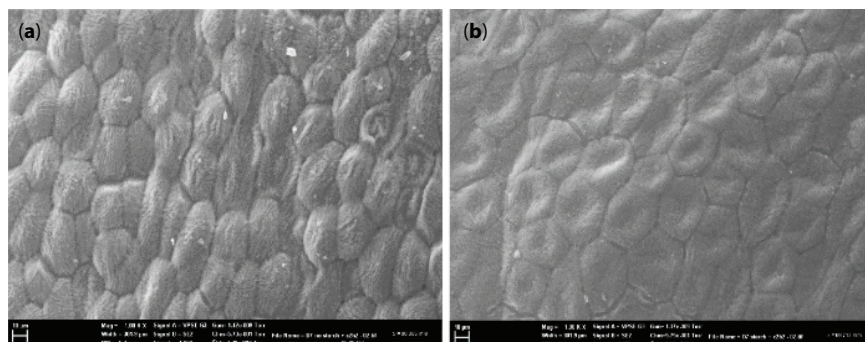


Figure 11.1 SEM micrographs of banana peel control (a) and coated (b) at 1,000× (Adapted from [31]).

Other major polysaccharide that is widely used in edible coating are alginates. Alginate is a polysaccharide derived from algae. Alginate represents alginic acid salts and its derivatives. The colloidal properties of alginates are ability to form gel and insoluble polymer when reacting with multivalent metal cations such as calcium [33]. Sodium alginate coated mango fruit shows higher antioxidant capacity than control fruit. Polyphenoloxidase activity in the coated mango remained lower than the control (uncoated mango) where it was observed to continuously increase [34]. The combination of sodium alginate with ascorbic and citric acids produced lesser browning on fresh-cut apples than pectin with same agents [35].

Chickpea starch, cassava starch, tapioca starch, corn starch, etc., are some of the other starches used for edible coating. The preservation of frozen dough and reduction in retrogradation rate are some emerging applications of the starch based edible coating [15, 36]. Different starches that are used for edible coating and its effect on the food quality are discussed in Table 11.1.

11.4.1.2 Cellulose Derivatives

Cellulose, the most abundant biopolymer that is present in all renewable sources such as wood, cotton, and plant-based materials, consists of a β (1-4) linked glucose residues [43]. Poor solubility and high crystalline nature of cellulose polymers make them difficult to use in packaging application. Poor water solubility of cellulose increases when soaked with alkali, swelling occurs, and reacting with chloroacetic acid, methyl chloride, or propylene oxide produces carboxymethyl cellulose, methyl cellulose, hydroxypropyl methylcellulose [44]. Therefore, the derivatives of cellulose including cellulose acetate, methylcellulose, hydroxypropyl methylcellulose, taurine cellulose are environmental friendly biopolymers, [45] filters, absorbents, and carrier material [1].

Methylcellulose and hydroxypropyl methylcellulose provide excellent barrier against gas transfer, but high moisture permeability [46]. These derivatives possess ability to form thermally stable coating, which is used for deep-fat frying products [47]. The principle of the thermally stable coatings was due to the methylcellulose and hydroxypropyl methylcellulose compounds exhibits thermo-gelation behavior [23]. This behavior occurs when suspensions are heated leading to formation of gel that returns below its gelation temperature, and viscosity is recovered [48].

Potato strips coated with methylcellulose reduces the oil absorption in the fried product around 40% without modifying the oil properties [49]. Similar results has been reported for reduction in oil uptake for fried potato chips [50], snacks [51], and chicken nuggets [52]. Hydroxypropyl

Table 11.1 Starch-based coating application on horticulture produce.

Biopolymers	Product	Inference	References
Rice starch, l-carrageenan, fatty acid esters of sucrose	Banana	Reduced weight loss, improved firmness, reduced starch degradation, and shelf life prolonged to 12 days from 6 days	[31]
Sodium alginate	Mango	Delay in weight loss, maintained higher concentrations of total phenolic compounds, and exhibited higher antioxidant enzyme activity	[34]
Cassava starch	Prickly pear	Delayed weight loss, softening and wilting of the fruit	[37]
Chickpea starch, stearic acid	Fresh-cut papaya	No weight loss and reduced microbial growth	[30]
Tapioca starch, natamycin, nisin	Gouda cheese	Protected against <i>Saccharamyces cerevisiae</i> and <i>Listeria innocua</i> . Maintained physicochemical properties	[38]
Rice starch, l-carrageenan, fatty acid esters of sucrose	Plum	Delayed respiration rate and retards the ethylene production	[32]

(Continued)

Table 11.1 Starch-based coating application on horticulture produce. (*Continued*)

Biopolymers	Product	Inference	References
Corn starch modified with ascorbic acid, tomato powder	Frozen bread dough	Bread with greater specific volume and less hardness	[15]
Waxy corn starch, gellan gum, sodium alginate	Rice cakes	Reduced retrogradation rate and hardness	[36]
Mango kernel starch, glycerol and/or sorbitol	Tomato	Retention of weight loss and firmness	[39]
Sodium alginate, pectin, ascorbic acid, citric acid, calcium chloride	Fresh-cut apple slices	Reduced microbial spoilage and wounding stress	[35]
Sodium alginate and/or pectin	Blueberry	Glossiness increased with decrease in lightness and increased blue hue color. Significant reduction in yeast and mesophilic aerobic bacteria.	[40]
Cassava starch, propolis extract	Strawberry	Maintained the higher free radical scavenging percentage and retained Vitamin-C content	[41]
Sodium alginate, ascorbic and citric acids (anti-browning agents)	Mango cubes	Ascorbic acid added coating shows color retention with enhanced antioxidant activity	[42]

methycellulose coated chicken balls showed reduced fat content (up to 33.7%) after frying [53]. Methylcellulose coatings were more efficient in oil reduction than hydroxypropyl methylcellulose coatings [54]. During frying, coating dehydrates and deposits at the food surface, which inhibits oil absorption and creates a compact network [23].

Hydroxypropyl methylcellulose is a cellulose derivative in drug release applications due to its high hydrophilicity and non-toxicity. Major application includes controlled release, under hydration, a gelatinous layer forms through which active compound releases [55]. It is difficult to use as a stand-alone coating matrix. To overcome this drawback, additives mostly lipid components, namely, waxes, triglycerides, and fatty acids, are incorporated into the biopolymer matrix. This addition acts as barrier to moisture migration and decreases the water affinity of hydroxypropyl methylcellulose [56].

Addition of beeswax into hydroxypropyl methylcellulose matrix was one of the most significant approaches in edible coating application. Beeswax tightly packed the available crystalline structure and makes the hydroxypropyl methylcellulose more hydrophobic [57]. The hydroxypropyl methylcellulose-beeswax (20%) coated guava fruit extended the conservation time of the fruit to six days more than uncoated control fruit, with reduced respiration rate and transpiration processes. The coating acts effectively in maintaining the color and firmness of the fruit [58]. Plums coated with hydroxypropyl methylcellulose-beeswax formulation show reduced weight loss, softening, and bleeding. Also increase in beeswax ratio in the coating reduced film flexibility and increased plum bleeding [59]. Therefore, it is necessary to optimize additives ratio in coating matrix. This formulation produces similar result for cherry tomato [60], "Ortanique" mandarins [61], "Valencia" oranges [62], and plums [63].

11.4.1.3 Gum

Gums are a class of natural polysaccharides or carbohydrate polymers derived from renewable sources that have the ability to form gel or stabilizing emulsion system. Gum coating provides a semipermeable barrier to the food products, which cause reduced respiration rate, weight loss, and maintain the nutritional value. It can act as a carrier of plant extracts, essential oils, phenolic compounds, and vitamins to improve the mechanical, antioxidant, and antimicrobial activities [64].

Gellan gum is a water-soluble anionic polysaccharide extracted from *Pseudomonas elodea* through fermentation process. It consists of repeating units of [β -1,3-D-glucose, β -1,4-D-glucuronic acid, β -1,3-D-glucose, α -1,4-L-rhamnose], and two acyl units, acetate and glycerate linked to the

glucose residue at the side of glucuronic acid [65]. It forms gels even at low concentrations when hot solutions are cooled in the presence of gel promoting cations [66]. This property helps to reduce the setting time of starch confectionary and prevents the sticky nature of candies when exposed to warm environment [67]. Fish pieces that are deep-fried with gellan gum coating reduced the fat absorption by 63% [68]. Similar reduction in fat absorption was observed for low fat pastry mix [69].

Guar gum is a water-soluble polysaccharide extracted from the legume plant, *Cyamopsis tetragonolbus*. It provides high viscosities in aqueous solution even at low concentrations [70]. It is a galactomannan consisting of mannose [(1→4)-linked β-D-mannopyranose] backbone with galactose side groups [(1→6)-linked α-D-galactopyranose] [71]. It is a type of soluble dietary fiber, which is effective in reducing glycemic index of various products especially bread made with guar gum shows similar sensory and lower insulin production than control bread [72].

Xanthan gum is an exopolysaccharide synthesized by *Xanthomonas campestris*, which forms high viscous in cold and hot water at low concentration with excellent stability over a wide range of pH and temperature. It also shows resistance to enzymatic degradation [66]. The structure of xanthan gum consists of pentasaccharide units composed by glucose, mannose, glucuronic acid in the ratio of 2.8:2:2 [49]. The effect of xanthan gum coating enriched with citric acid and ascorbic acid on grapes explains the chelating effect exerted by citric acid in the coating, depletes the copper ion availability to polyphenoloxidase, and suppresses the enzyme activity [73].

Gum Arabic also known as acacia gum is the tree gum exudates of *Acacia senegal* and *Acacia seyal*, consists 1,3-linked β-D-galactopyranosyl units linked through 1,6-linkages [74]. It is the most used gum in fruits and vegetable coating [64]. Other gums that are used for edible coatings are karaya gum (*Sterculia urens*), tara gum (tara tree), peach gum (peach tree), cashew gum (*Anacardium occidentale*), flaxseed gum (*Linum usitatissimum*), tragacanth gum (*Astragalus gummifer*), and almond gum (*Amygdalus communis*). The effect of gum based edible coatings on different fruits and vegetables are tabulated in Table 11.2.

11.4.1.4 Protein

Proteins are hetero biopolymers, composed of 20 α-amino acids in addition to the amino and carboxyl groups involved in the formation of peptide bonds that contain side chains. These can be electrically charged or uncharged and either hydrophobic or polar, and each amino acid exhibits distinctive characteristics [91]. The primary structure of the protein

Table 11.2 Gum-based edible coatings of foods.

Biopolymers	Product	Inference	References
Xanthan gum, ascorbic and citric acids, glycerol	Grapes	Reduced polyphenoloxidase, ascorbic acid oxidase, and pectinmethylesterase enzyme activities.	[73]
Gum Arabic	Strawberry	Inhibited polyphenoloxidase activity, reduced decay percent, and delayed physicochemical changes.	[75]
Tragacanth gum, ascorbic acid	Fresh-cut apple slices	Inhibited polyphenoloxidase activity, retained ascorbic acid, and total phenol contents.	[76]
<i>Cajanus cajan</i> seed gums	Strawberry	Reduced citric acid consumption and physicochemical changes during storage.	[77]
Xanthan gum	Guava	Maintained ascorbic acid and polyphenol contents and reduced respiration rate.	[78]
Gum Arabic, tulsi extract	Guava	Reduced ripening and senescence. Inhibited mold growth.	[79]

(Continued)

Table 11.2 Gum-based edible coatings of foods. (*Continued*)

Biopolymers	Product	Inference	References
Gum Arabic, <i>Origanum vulgare</i> and <i>Rosemarinus officinalis</i>	Plum	Protected the soft rot incidence and phenolic compounds were retained	[80]
Gum Arabic	Raw and blanched tomatoes	Water activity, browning index and rate of increase in dry matter were reduced	[81]
Trangacanth, almond, quince seed gums	Banana slices	Reduced shrinkage and inhibited browning index	[82]
Flaxseed gum, lemongrass oil	Pomegranate	Reduced microbial growth and delayed physicochemical changes during storage	[83]
Peach gum	Cherry tomato	Retarded changes in sugar, ascorbic acid and acidity and reduced respiration rate	[84]
Gellan gum	Mango bars	Preserved color and volatiles with improved firmness and appearance	[85]
Gum Arabic, ginger oil/ginger extract	Papaya	Served as biofungicide for controlling anthracnose	[86]
Guar gum, cinnamon oil, potassium sorbate	Cucumber	Improved antioxidant and antibacterial activities	[87]

(*Continued*)

Table 11.2 Gum-based edible coatings of foods. (*Continued*)

Biopolymers	Product	Inference	References
Guar gum	Fried potato chips	Reduction in oil adsorption and crack formation	[88]
Almond gum	Fried potato chips	Improved color, texture, and sensorial characteristics	[89]
Xanthan gum, cinnamic acid	Fresh – cut pears	Inhibited polyphenoloxidase and peroxidase enzyme activities and retards oxidative browning	[90]

depends on its specific polypeptide chain and the spatial orientation of these chains is the secondary structure. The tertiary structure indicates the three-dimensional organization of the polypeptide chains to form globular, fibrous, or randomly coiled conformations. The quaternary structure depicts the result of interaction between different polypeptide chains that determines the final protein structure [92].

Proteins are classified into two types—globular and fibrous. The first one is soluble in water or aqueous solutions of acids, bases, or salts. The folded spherical structures of globular proteins are held by a combination of hydrogen, ionic, hydrophobic, and disulphide bonds. Wheat gluten, soy protein, corn zein, and whey protein are some of the globular proteins used for edible coating. The latter one is insoluble in water and structural element for the animal tissues. Collagen is a major fibrous protein used in edible coating. However, plant proteins are grouped into four categories—albumin (water-soluble), globulin (soluble in saline solutions), prolamine (soluble in aqueous alcohol), and glutelins (extractable in alkali) [93].

The denaturation of the protein structure is the necessary step to unfold the chains for network formation. The chain-to-chain interactions of protein molecules made the polymer matrix stronger and less permeable to gases and vapors [94]. Proteins have multiple sites for chemical interaction that permits property improvement and tailoring [95]. The intrinsic properties of the coating components and extrinsic processing factors affect the coating performance [96]. Intrinsic properties of proteins include amino

acid composition, crystallinity, hydrophobicity/hydrophilicity, surface charge, Iso-electric point, molecular size, and three-dimensional shape. Processing temperature, drying conditions, pH, ionic strength, salt-type, relative humidity during processing and storage, shear and pressure are the extrinsic factors affecting protein based edible coating [91].

Zein is also known as the storage prolamine protein of corn. It consists of high amount of leucine, alanine, and other non-polar amino acids, which makes them water-resistant and thermoplastic [91, 97]. Zein is insoluble in water. The two major fractions are alpha-zein and beta-zein, which dissolves in 90% and 60% ethanol [97]. The formation of hydrophobic, hydrogen, and limited disulphide between the zein chains makes them an excellent biopolymer [98].

Gluten is the wheat protein consists of two insoluble portions—gliadins and glutenins. It consists of a large amount of non-polar amino acids and small portion of charged amino acids such as lysine, histidine and arginine that enhances the protein aggregates through hydrophobic interactions [99]. The disulphide bonds present in glutenin and gliadin determine the strength of protein matrix [100].

Soy protein is the globulin protein fraction of soybean. This protein consists of both polar and non-polar side chains. Soy protein exhibits strong intra- and inter-molecular interactions, such as hydrogen bonding, dipole-dipole, charge-charge, and hydrophobic interactions [101]. The two main globular proteins are glycinin (11S-globulin) and beta-conglycinin (7S-globulin) [102]. The denaturation of glycinin forms intermolecular disulphide bonds that affects the mechanical strength of protein matrix [103].

Moreover, the cross-linking between protein chains enhances the protein network formation and improves the stability of the matrix. Thermal treatment [104], irradiation [105], enzymatic and chemical cross-linking [106, 107] induce various bond formations and improve the tensile strength and barrier properties of the coatings. The recent literature survey depicts a high number of publications related to the application of soy protein, in one or the other form, as the basis of the coating (Table 11.3).

11.4.1.5 Waxes

Wax represents a series of naturally or synthetically produced non-polar substances. Wax consists of zero or little polar compounds that are hydrophilic, so that these compounds cannot interact with water molecule. This nature possesses difficulty for the wax compounds to spread and forms thin layer over food product. Wax coatings have been reported to exhibit strong resistance to moisture migration. Though, irregular thickness,

Table 11.3 Recent studies with application of plant proteins as potential coatings.

Biopolymers	Product	Inference	Reference
Soy protein isolate, honey (dip)	Fresh-cut pineapple	Shelf life extended (2 weeks), retention of phenolic compounds and color	[108]
Soy protein isolate, honey (dip)	Fresh-cut kajari melon	Reduced microbial growth with better sensory scores	[109]
Zein, tannic acid	Guava	Maintained fruit quality attributes, extended stability, and reduced gas exchanges	[110]
Soy protein isolate, chitosan	Apricot	Prevented weight loss, softening, and pectin degradation	[111]
Soy protein isolate, ferulic acid	Fresh-cut apple	Controlled weight loss and firmness	[112]
Soy protein isolate	Beef patties	Delayed lipid oxidation, maintained color deterioration and texture	[113]
Soy protein isolate	Potato pellet chips	Reduction in oil uptake and improved sensory characteristics	[114]
Zein, tannic acid	Guava	Maintained fruit quality attributes, extended stability, and reduced gas exchanges	[110]
Zein, hazelnut skin extract, α -tocopherol	Hazelnut	Reduced oxidative rancidity in the roasted product without any quality changes	[115]
Zein, polymeric chelator	Fish balls	Retards the bacteria growth and extended shelf life	[116]

greasy surfaces, and unacceptable taste of fat are the limitations to the application of wax coating [117].

Carnauba wax is a natural plant wax extracted from Brazillian palm tree (*Copernicia cernifera*) [118]. The carnauba wax and carnauba wax with glycerol monolaurate coated Indian jujube shown in Figure 11.2 explain that the wax coating inhibits the chlorophyll degradation and slows down the respiration rate in the day 8 and 12 of storages when compared with control (uncoated) fruit [119]. The increase in redness during storage indicates the jujube ripening, senescence, and chlorophyll degradation in uncoated fruit.

In a study conducted, it was observed that the preservation of fruits through antagonistic microorganism such as fungi, yeast, and bacteria with inactivating mechanisms of competition of nutrients and niches, antibiosis, lytic enzymes, volatile inhibitory metabolites, pH decrease, and parasitism were possible [120]. The strawberries coated with candelilla wax and *Bacillus subtilis* HFC 103 biocontrol agent showed significant severity index against *Rhizopus stolonifera* and completely restricted the fruit decay till 6 days of storage [121].

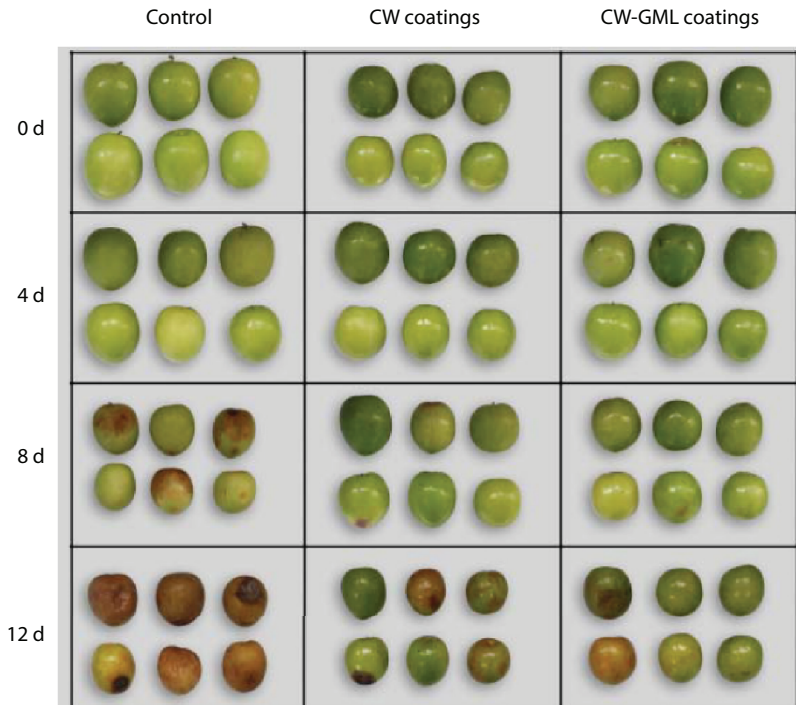


Figure 11.2 Control, carnauba wax (CW) coated, carnauba wax-glycerol monlaurate (CW-GML) coated Indian jujube fruits at 0, 4, 8, and 12 day of storage [119].

Lacquer wax is a fatty acid resource present in the mesocarp and seed of the berries from the Chinese tree *Toxicodendron vernicifluum*. It is consisting of hexadecadienoic acid, eicosenoic acid, and dodecadienoic acid. Therefore, lacquer wax was more elastic and softer than other waxes [122]. It is cheap, abundant, natural, edible, and easy to prepare. The lacquer wax coated kiwifruit slows down the respiration rate and retards the activity of pectinmethylesterase and polygalacturanase activities [123]. The different wax coated fruits and vegetables are depicted in Table 11.4.

Table 11.4 Recent application of wax as an edible coating.

Biopolymers	Product	Inference	References
Carnauba wax, glycerol monlaurate	Indian jujube	Glossiness maintained, reduced chlorophyll degradation	[119]
Lacquer wax	Kiwifruit	Suppressed the respiration rate, ethylene production and fruit softness	[123]
Carnauba wax, galactomannan	Guava	Reduced chlorophyll degradation and prevented from chilling injury	[124]
Candelilla wax, <i>Bacillus subtilis</i> HFC 103 (biocontrol agent)	Strawberry	Reduced fruit decay, protection against <i>Rhizopus stolonifer</i>	[121]
Candelilla wax, pectin, aloe mucilage	Avocado	Inhibited internal grey pulp development	[125]
Carnauba wax	Eggplant	Reduced physiological weight loss, enhanced antioxidant activity of eggplants	[126]
Candelilla wax, fermented extract of tarbush	Apple	Maintained firmness, retained sensory scores	[127]

11.4.2 Animal Source

11.4.2.1 Chitosan

Over the past decade, the focus of the marine processing industry has been directed towards the utilization of its waste in a feasibly better and creative way to cater the generated carbon footprints during the processing of the waste. One of these was the utilization of crustacean shells, which accounts for a high volume of waste that is being developed during the in shellfish processing [128]. This waste cannot be consumed directly for food purposes, but with deliberate use of processing can prove vital in several applications, one of which is developing it as an edible coating.

Chitin, the abundantly found biopolymer in the exoskeletons of these in-shell crustaceans, is structurally identical to cellulose. Chitosan, which turns out to be a copolymer of β -(1-4)-2-amino-D-glucose and β -(1-4)-2-acetamido-D-glucose, is the deacetylated form of chitin, which is known for the antimicrobial properties related to its cationic and film-forming properties [129]. Several *in vitro* trials on various food matrices have proved its ability to act as a natural food preservative. But the fact that chitosan coatings are highly permeable to water vapor limits, its use since control over the moisture is the most desirable characteristic of the coatings being used for foods stored in moist environment [130]. Hence, still extensive studies are needed to cater the limitations of chitosan to be used as a coating alone.

In the aforementioned context related to drawbacks of chitosan, investigations have been carried out depicting the increase in hydrophobicity by the inclusion of neutral lipids, waxes, and certain clays [131], whereas some chemical and physical alterations (methylated or sulfated polylactic acid) are also being utilized for increasing the mechanical properties by the means of ultrasound, irradiation, and crosslinking agents.

The outbreak of microbes in the processed food processing industry is the major concern lurking over the food processors to store and monitor the frozen fruits and vegetables and even the fresh-cut meat and poultry flesh [132–134]. The antimicrobial activity of chitosan leads to a leakage of intercellular constituents and provokes the osmotic imbalance, resulting in the growth inhibition of the particular microbe. It's fascinating to observe a high number of publications (over 2,038) related to chitosan and its characteristic activity which is due to the physicochemical and biological attributes, out of which several supports the use of chitosan as edible coatings and even as films. There's no study till date which can describe the

exact mechanism of microbial inhibition due to the antimicrobial activity of chitosan but many proposals are in line to depict the same. Some of the applications for the shelf life prolongation or preservation of different food matrices are compiled in Table 11.5.

Table 11.5 Recent studies on chitosan-based edible coatings.

Effect	Products	Added value	References
Antioxidant/Antimicrobial Activity	Blueberry	Extended shelf life of 5 days	[135]
	Cherry Tomato	Control over mycelial growth and fungi	[136]
	Cucumber	Control of <i>Phytophthora Drechsleri</i> with extended shelf life of 21 days	[137]
	Table Grape	Delayed mold growth (<i>A. niger</i> , <i>P. expansum</i> , and <i>R. tolonifera</i>)	[138]
Sensory Enhancement	Mango	Increased flesh firmness	[139]
	Star Fruit	50% extended glossiness with shelf life of 40 days	[140]
	Bamboo Shoot	Inhibited activity of PPO and peroxidase	[141]
	Litchi	Lower hydrogen peroxide and MDA content	[142]
	Pumpkin	Control over PPO and POD release	[143]
Preservation (Cheese)	Ricotta	Retained sensory attributes with enhanced shelf life up to 30 days and control over majorly affecting micro-organism (<i>Listeria innocua</i> , <i>Escherichia coli</i> , and mesophilic aerobic bacteria)	[144]
	Mozzarella		[145]
	Saloio		[146]
	Cheddar		[147]
	Soft white		[148]

(Continued)

Table 11.5 Recent studies on chitosan-based edible coatings. (*Continued*)

Effect	Products	Added value	References
Preservation (Meat and other products)	Shrimps	17 days shelf life with control over <i>Pseudomonas</i>	[149]
	Chicken Breast	Postponed oxidative deterioration and enhanced shelf life of 10 to 15 days	[150]
	Beef Fillets	30 days prolonged shelf life	[151]
	Dry fermented sausages	Better odor and flavor characteristics with notable increase in stability of the sausage core	[152]
	Beef steaks	21 days shelf life with reduced drip loss	[153]
	Rainbow trout fillets	22 days shelf life with control over coliform count	[154]

11.4.2.2 Animal Protein

11.4.2.2.1 Gelatin

Coming on to the meat processing industry, gelatin is one of its derivatives from the collagen which is extensively being used as a biopolymer for its impressive functional properties. As it comes under the section of protein-based biopolymer, it possesses 3-D structures governed by the several interactions, among them, the major are non-covalent forces [155]. The use of such polymer as a coating for highly perishable commodities like meat and fish cuts depends on the cost, availability, mechanical capacity, and its optical characteristics.

During the 1930s, pigskin was among the first materials been used to manufacture the gelatin and it still holds a large percentage of production under its use in the large-scale food production; else gelatin is also obtained from cattle bones but it comes out to be a more complex and costly method when compared with the former [156]. Apart from porcine and bovine gelatine which comes under the category of the meat derived gelatin, the utilization of fish gelatin is also on a high during the recent times, but only accounts to a mere 1.5% of the total production [157].

The attributes of the gelatin being manufactured are primarily based on the characteristics of initial collagen and on the extraction process, up to some extent. The process onsets from the warm water extraction, destabilization of the hydrogen, and the covalent bonds and terminates with the subsequent conversion into its solubilized form. The structural skeleton of gelatin consists of a polymeric α -chain, two covalently cross-linked α -chains which eventually give rise to a β -chain, and γ -chains. Gelatin's amino acid structure follows the trail as: Ala-Gly-Pro-Arg-Gy-Gly-4Hyp-Gly-Pro- (Figure 11.3). The main property because of which the use of gelatin has gained importance is the gel strength (or known as bloom value) it develops that also enables us to use it in the powder and granulated form [158].

Gelatin has a wide application with film-forming capacity as one of the well-known attributes. It has been studied extensively for its ability to protect the food from getting dried and from the exhibition to light and exposure to oxygen. But alongside substances like cross-linkers, plasticizers, oils, and other additives, gelatin coatings have overcome all its drawbacks and provided better stability to the food products [159]. It can even be seen in some literature that the use of gelatin alongside other biopolymers like whey proteins, starch, pectin, and chitosan have proved to be a better strategy to refine its mechanical and water resistance properties [160]. But when it comes to the utilization, major reported publications are for the

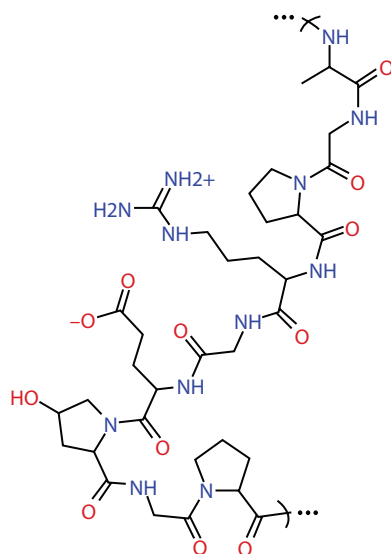


Figure 11.3 Amino Acid Skeleton of Gelatin.

casting of films and use of gelatin for the purpose of coating lies still in its making [161].

Unlike chitosan, Shakila, Jeevithan [162] claim the enhancement of antimicrobial properties and shelf stable product for fish steaks by the use of grouper bone gelatin when used with the clove and pepper essential oil as additives. This depicts the strength and the effect of the additives in the formation of the coating. Similarly, Wu, Liu [163] suggest the application of fish gelatin for the purpose of encapsulation for the monitored delivery of the active compounds. Here, also the formulation was incorporated with essential oil (cinnamon) to enhance its properties. Food grade gelatin has also been reported to be used for coating shrimps, incorporated with orange peel essential oil for an edge with the increased antioxidant activity [164]. Different matrices of gelatin are used as coatings for the various meat and fishery and horticultural produce in recent years (Table 11.6).

Table 11.6 Recent literatures with the application of edible gelatin-coating.

Product	Coating	Method	Reference
Nile tilapia fillets	Fish scale gelatin + Chitosan	Dipping in formulation matrix	[165]
Beef meat	Fish gelatin + Pectin		[166]
Hake medallions	Fish gelatin + Carvacrol		[167]
Strawberry	Gelatin + Mentha oil		[168]
Pastirma	Gelatin + Alginate		[169]
Tuna fillet	Gelatin + Chitosan + Clove oil		[170]
Beef steaks	Gelatin + Pectin + Sodium alginate		[171]
Shrimps	Gelatin + glycerol + Tween 20 + sorbitol + orange leaf extracts		[164]
Raw Beef	Gelatin + Tween 80 + Thyme & Rosemary oil		[172]
Pork loin	Pork gelatin		[173]
Kabanosy dry sausage	Porcine gelatin + Kappa-carrageenan + Glycerol		[174]

11.4.2.3 *Milk Protein: Whey and Casein*

Milk protein contains various essential components that make it relevant to be used as a biopolymer. Casein is found abundantly in the ruminant's milk proteins while the cow's milk gives around 18% of the whey protein.

The micelle structure of the casein yields to form spherical complexes which are colloids of calcium phosphate. This paves way for the utilization of the film-forming property of the casein protein in order for edible coating over the perishable food commodities. Here, the method of extraction governs the solubility of the film being produced. Coatings with essential oils from the *Zataria multiflora* and ginger rhizomes have been successfully deployed for the shelf life extension of certain food commodities. Now, coming on to the whey protein, which is developed during the cheese production, the principal compound present deals with the properties which are the key to make the whey protein cater as a coating material.

Under the classification, the Whey Protein Isolate (WPI) and Whey Protein Concentrates (WPC) are the most widely used as coating materials. Literatures reported for the application of coating onto the roasted peanut kernels [175], cut apples [176], pike-perch fillets [177], and even on carrots claims the efficacy of WPI as an effective coating material. WPI also depicted wonderful results when used under modified atmospheres and vacuum packaging for tuna [178]. Blended formulations also have proved beneficial in the past as Catarino, Alves-Silva [179] reports the use of cinnamon and rosemary essential oils applied on the sausages for its manufacturing. This was supervised for a period of four months and even proved beneficial in delaying microbial spoilage and preventing discoloration.

11.4.2.4 *Shellac*

Shellac is a natural biopolymer being prepared by the *Kerriar lacca* insect's secretions, which is popular in some of the South Asian countries including Thailand, India, and China. It mainly consists of a combination of hard and soft resins and single ester with polyhydroxy-polybasic acids, *viz.*, laccijalaric, jalaric, and aleuritic acid [180]. This is gaining interest in recent times due to its excellent protection against the moisture and because of its exceptional glossy finish films and its properties that are produced on the surfaces [181]. This may be used as a singly or can be formulated for combinations also. The sole purpose of this intervention in the shellac's formulation is to control the permeability of the coating for delaying the senescence process of the agricultural produce [182]. This primarily affects

the oxidizing enzymes that govern the ethylene production, moisture loss, and the firmness of the commodity. But, shellac is also prone to the instability caused because of polymerization thus reducing its mechanical strength; therefore, the need of modification arises while using the shellac. Thus, research on the best possible formulation can be done with the efficiency of coating in mind and can be further optimized to ensure high marketability [183].

The coating which was being used until the introduction of shellac had many limitations which direct emphasis on the quality which is reflected on the stability of the product. Polysaccharides, as well as the proteins, could not handle the situations as the issue of low moisture protection persisted. The lipid coatings, due to their low polarity, gave high moisture barrier but their low cohesiveness laid down the difficulty in the formation of independent polymer [156]. Thus, this formed a gap to be filled by a hydrophilic polymer to improve the weakness against the moisture, and thus, the use of shellac began with the polysaccharides and protein-polymer [180].

Saberi, Chockchaisawasdee [184] depicted the utilization of shellac while formulating homogenous layer of the pea starch/guar gum along with Tween 20. Other studies published regarding the combination of carnauba wax and shellac alongside lemongrass oil for coating apples also had a high impact. The coated apples had lower count of yeast and molds with even emergence of bacteria was reduced to an extent [185]. Later, Soradech, Nunthanid [186] investigated the delay in ripening characteristics of banana on using the shellac-based composite coating. This ended up increasing the shelf life with the quality parameters retained which were monitored on the color profile of the surface of the banana (Figure 11.4).

11.5 Composite Coatings

Composite coatings consist of two or more biopolymers that form the network together to overcome the limitations of individual component. Composite coating exhibits the advantage of each biopolymer and produces unique characteristic coating. Polysaccharide-polysaccharide, protein-protein, polysaccharide-protein, polysaccharide-lipid, and protein-lipid are the different blends that are used for composite edible coatings.

Potassium sorbate, organic salt of sorbic acid, holds scope as effective fungistatic agent in perishables. Kowalczyk, Kordowska-Wiater [187] developed a composite coating for fungus infected apricots, coating

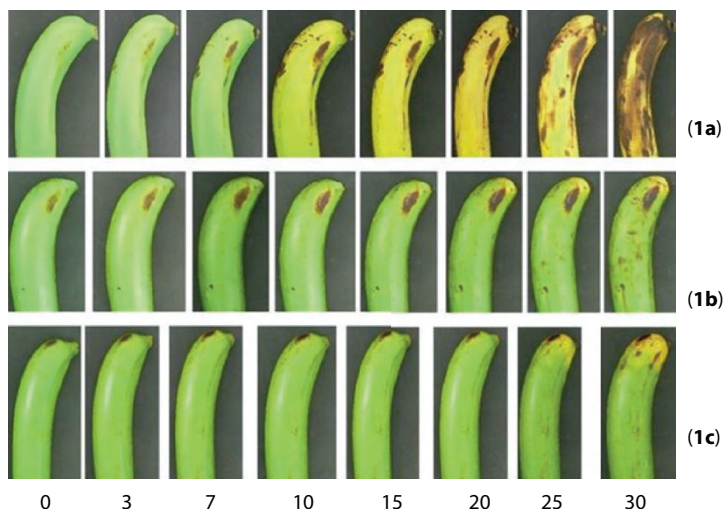


Figure 11.4 Color profile of banana without coating (1a), with shellac coating (1b) and with the formulated composite film (1c). (Adapted from [186]).

consists of carboxymethylcellulose and candelilla wax blend with and without potassium sorbate. *Botrytis cinerea* and *Monilinia fructigena* were the most sensitive to the antifungal treatment. The significant reduction in oxygen consumption was observed for the coated apricots, which in turn relates with the controlled enzyme activity and softness of the fruit.

Nano polymeric materials can have an edge in the delivery and retaining the bioactive in the food matrix. They are generally introduced into a polysaccharide or protein matrix to form a mixture of particles for the purpose of coating with at least one of the component in the nanoscale. This is also known as “temporal distribution system” that may release the active component at the time of storage. These can be used in the form of nanoemulsion, polymeric nanoparticles, solid lipid nanoparticles (SLNs), lipid nanocarriers, inorganic/organic nanocomposites, and even as nanotubes and nanofibers with direct application on the food surface (Figure 11.5).

The micro-fibrillated carrot was coated with starch as biopolymer in order to have an extended shelf life. The bioactive acted as a medium to strengthen the coating's mechanical property and its functionality and compatibility [189]. Similarly, chitosan coating reinforced with the cellulose nanofibers (CNF) (manufactured in the name of Avicel®) improved the glass transition temperature and its vitreous nature [190]. Wang, Liu [191] reported that CNF was used along with the fish gelatin and palmitic acid

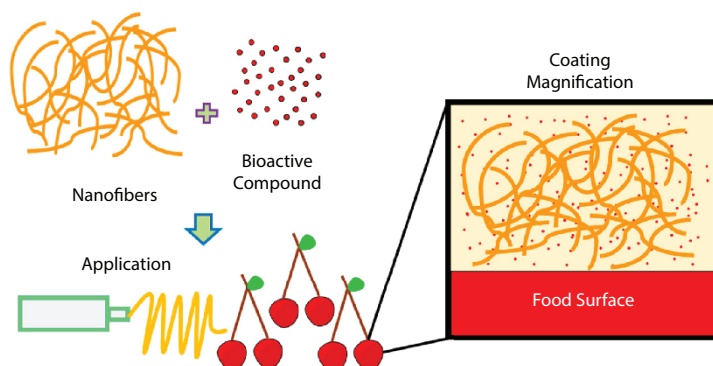


Figure 11.5 Schematic representation of nanofiber application as coating (Adapted from [188]).

formulation to increase resistance against the gases as well as the strength up to some extent. In another reported study, the bioactive compound from the turmeric rhizomes, curcumin, encapsulated in zein nanofiber was used to coat apples for improving its shelf stability. The surface of these apples was inoculated with *Penicillium expansum* and *Botrytis cinerea* to check the efficacy of the composite coating which was electrospun over the surface of apples. The use of nanocomposite coating successfully inhibited the microorganisms for a fortnight's time [192]. Cui, Yuan [193] developed a composite with mounted bacteriophage, encapsulated in lysosomes for a controlled release, to counter the microbial attack on stored beef. This composite assembly was mounted on the chitosan and the product came out to be a very efficient antibacterial coating without affecting the sensorial characteristics of beef (Figure 11.6).

11.6 Current Trends

Bionanocomposites consist of reinforced matrices with organic or inorganic (nanoparticles) with a 1-D nano structure (1–100 nm). Conventional microscopic fillers present poor interaction at the interface, while nanofillers present better interaction between both phases due to high surface/volume ratio [194]. These materials exhibit improved thermal, mechanical, and barrier properties due to the high aspect ratio and the surface area of the particles formulated. The properties of these composites are judged by the range of the dispersion of nanoparticles in the biopolymeric structure and by the interaction within them [195].

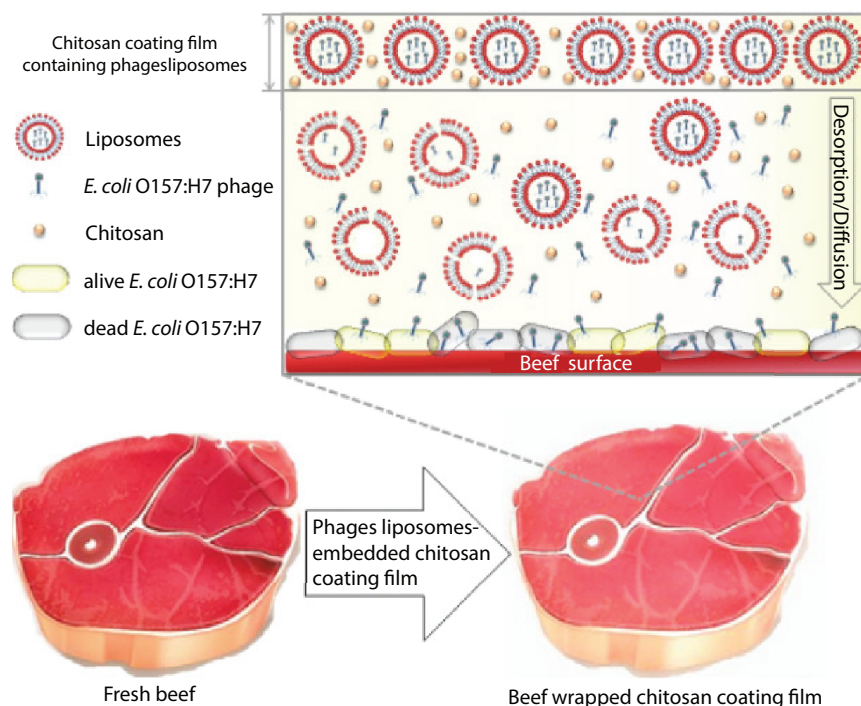


Figure 11.6 Schematic representation of antibacterial composite coating of chitosan on beef (Adapted from [193]).

Edible coatings, with time, has changed the use and perception associated with the biopolymers for food coatings. With inclusion of nanomaterials, the reach of supplying the materials that are essentially needed has increased with a tremendous rate. The bioactive which earlier were considered to be ingested only by its natural source can now be coated in the biopolymer and delivered to a pre-known targeted site [196]. But, evolution follows the invention, and thus, there remains a need for improvement in a particular entity and its methods to be used, always.

In the case of coatings, such changes are being brought up by making the coatings self-able, so that it can detect any deliberate change occurring during its presence over the particular food commodity. This calls for the development of smart or active coatings. This is a novel approach towards monitoring the horticultural produce. It makes use of immobilized nanoparticles (antimicrobial, at times) and has the capability to monitor the internal gas composition and to cease the ethanol fermentation. These coatings can also be as self-adhesive coatings which are able to communicate with the end consumer about its state and condition at the time

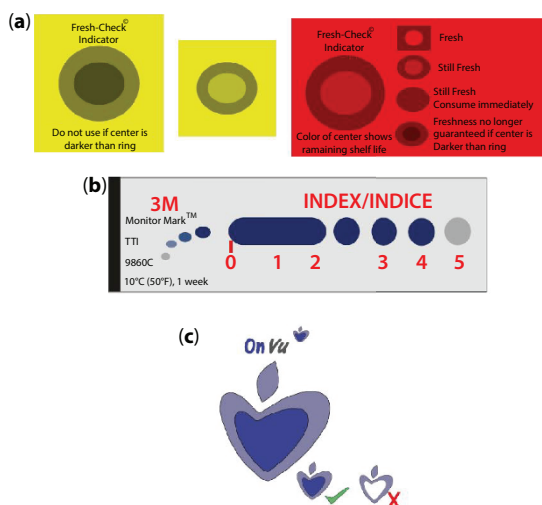


Figure 11.7 Commercially available indicators; (a). Fresh-check® label; (b). Monitor Mark™ label; (c). OnVu™ label (Adapted from [198]).

of ingestion. This also turns out to be a helping technique which can contribute to improving the HACCP and QACCP systems [197]. These sensors can be used as indicators and data carriers wherever it fits the purpose and indicates the possible attribute which is being monitored to check the quality. Figure 11.7 illustrates one of the fine examples of such techniques commercially being used nowadays.

Secondly, the next most talked about technique in recent time is the layer-by-layer or L-B-L coating technique which uses different biopolymers themselves to overcome the drawback of the others [199]. This limits the use of synthetic additives and makes our aim towards green manufacturing up to some extent. It consists of formation of groups of sequentially adsorbed complementary molecules which yields the formation of multilayer coatings. It is better than the earlier used Langmuir-Blodgett and self-assembled monolayer techniques which needed expensive machinery and amphiphilic materials [200]. Its applications span from its use in sensors, drug delivery systems, catalysis and to even in the energy storage and conversion [201].

11.7 Conclusion

In accordance with the industrial and substantial viewpoints, biopolymer coatings are the future materials in the processing industry. Several naturally occurring biopolymers are being used to produce shelf stable and self-able

composite for the purpose of coating of the food commodities. However, it is critical to realize the reason that biopolymer coatings can become a mandate luring with time due to its attributes. The general need of novel fabrication and the nanomaterials can help in the betterment of the known barrier (to water, oxygen, and UV/light) properties of such coatings. Notably, this can implement unique features with add-ons in biopolymer films, opening a medium of novel applications for food industry. However, the perniciousness, Geno-toxicity, and neurotoxic effects are not exonerated till date. So, it becomes important to focus the studies towards the nanoparticle migration into meat, fish, and even beverages with its risks accompanying furthermore possible intake, before the nanoparticle application in industrial packaging. Moreover, government assistance in the emerging countries and reducing a huge cost leap in comparison of biopolymers to that of the plastic polymers are the necessary factors to be considered, to increase the biodegradable packaging market.

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Polymer Coatings for Pharmaceutical Applications

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Abstract

Polymeric coating of pharmaceutical dosage form is one of the effective tool to improve the patient compliance, shelf life and therapeutic efficacy of drugs by providing protection against physical degradation, chemical degradation and unpleasant taste. Added advantage offers potential opportunities to modify the drug release characteristics. This chapter outlines the historical evolution of concepts and practices of coating pharmaceuticals for providing better drug delivery systems. The types of coatings for pharmaceutical products, primarily solvent-based coatings, solvent-less coatings and polymer coatings for micro/nano particulate drug delivery systems, as well as mechanism of drug release through coating system are discussed. Pharmaceutical products utilizing such approaches and polymers range from simple coated tablets to those employing more complex technologies for nano particulate drug delivery systems. Technologies including self-organized/assembled coating, coating by coprecipitation, coating by adsorption and coating through layer by layer assembly are described.

Keywords: Polymer, pharmaceutical coating, solvent-based coating, solvent-less coating, nano particle coating, drug release mechanism

12.1 Introduction

The coating of pharmaceutical solid dosage forms holds multiple benefits such as masking of the unpleasant taste and odor, protection of the drug

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substances from oxidation, and degradation due to photo and pH sensitivity and thereby enhancing the stability of the drug substance. Moreover, the coating of solid drug products with polymers also helps in modifying drug release characteristics. Thin film coating also enhances the product appearance and helps in identification of the product. Furthermore, this also reduces the friction in high speed packaging machine for increasing the production output. The coating applications on solid dosage forms also facilitates its swallowing and may help reduce the interaction between two or more drug substances by forming polymeric coating layers in dosage forms [1–3].

12.2 Polymers for Coating Pharmaceuticals, A Historical Perspective

Coating of pharmaceutical products is more than a thousand-year-old practice. The first coating procedure was reported by Muhammad ibn Zakariya al-Razi (*Rhazes*) around 900 A.D. where he used mucilage of *Psyllium* seed for coating pills. Later on, Ibn e Sina (*Avicenna*) introduced gold and silver coating in pharmacy [4, 5]. In nineteenth century, pharmacists frequently used gelatin and sugar as a coating material for pills to mask the bitter taste. In 1884, German Physician, Dr. Paul Unna introduced keratin coated pills having resistance in a gastric environment with disintegration and dissolution characteristics in the intestinal medium [6]. Sugar coating was a dominant method till mid of the twentieth century, but due various reasons such as higher time consumption, less automation, higher batch-to-batch variation, the requirement of specialized skills, and a considerable increase in the final tablet weight resulted in a shift of practice to use polymer-based film coating instead in 1950s. As a result, the production run time did not only reduce from days to hours but also led to enhanced benefits such as improved tablet strength, aesthetic appearance, and easier swallowing with a higher level of patient compliance [7–9].

Modified release coating polymers such as cellulose acetate phthalate (CAP) was also introduced in 1951 for enteric coated drug delivery systems [10]. After CAP, hydroxypropyl cellulose phthalate (HP50 and HP55), hydroxypropyl methylcellulose (HPMC), and ethyl cellulose (EC) were introduced. These polymers and their mixtures have variable solubility characteristics in different organic solvents and pH. Disintegration time ranges from a few minutes to several hours also because of different

EC and HPMC proportions [11]. In 1953, Swintosky of Smith Kline and French used hydrogenated castor oil-EC combination for tablets and pellets coating. In the same year, Rohm and Hass marketed Eudragit®, copolymer acrylic acids, and methacrylic acid and their esters. Different Eudragit type L and S polymers were introduced with different ratios of acrylic and methacrylic acid at that time. Till date, at regular intervals, different other Eudragit type and grades are available from Evonik Industries [12]. In the 1970s, the efforts of Higuchi and coworkers at ALZA Corporation led to the discovery of osmotic drug delivery system whereby the drug is released from tablets or capsule through an orifice due to osmotic pressure. The cellulose acetate coated semi-permeable polymeric membrane on the surface allows water to move inside that causes the dissolution of the drug in an osmogen containing core [13–16]. The first tablet product based on ALZA “elementary osmotic pump” (EOP) Acutrium® was marketed by Ciba Geigy in the early 80s for delivering phenylpropanolamine [17].

Concept of coating hard and soft gelatin capsule was also introduced in the 1980s and was subsequently patented. The finished capsule shell was used to be subcoated with HPMC suspension. This subcoating, later on, was used for improved enteric coating on capsule shell. Murthy *et al.* in 1986 studied and compared coating Eudragit® L 30 D, Aquateric®, and Coateric® an aqueous enteric polymers on hard gelatin capsules shell. Eudragit® L 30 D-55 coating on soft gelatin capsule was also reported by Felton and her colleagues [18–20].

Dry coating, a type of solventless coating using hydroxypropyl methylcellulose acetate succinate (HPMCAS) as a novel enteric coating method, was developed by Obara *et al.* in 1999. Method reduced not only the processing time but also suitable for water sensitive materials [21]. Other solventless coating methods such as compression coating, electrostatic coating, hot-melt coating, supercritical fluid spray coating, and photocurable coating were also introduced for developing different controlled release products during this period and in early 2000 [22–30].

Nanoparticle polymeric coating for therapeutic purpose was another major development when nanoparticles coated with block copolymer, poly(oxyethylene)-poly(oxypropylene), substantially increased the time of blood circulation of delivery vehicles by reducing the liver and spleen uptake [31, 32]. These nanoparticles if uncoated were found to be rapidly opsonized and removed by the reticuloendothelial system of liver, spleen, lungs, and bone marrow [33–35].

12.3 Types of Coatings Used on Pharmaceutical Drug Products

There are two major categories of various procedures used to coat polymeric substances on the drug dosage forms and delivery systems. The first and most popular category comprises of solvent (aqueous/organic)-based coating procedures while the other is rest of the methods which doesn't use any solvent to disperse or dissolve the polymeric material.

12.3.1 Solvent-Based Coatings

Solvent-based polymeric coatings on pharmaceuticals are applied to various dosage forms available commercially such as tablets, capsules, and multiparticulate systems, e.g., pellets, etc., in solvent-based coating procedures usually a single or multiple coats of a solution or dispersion of polymeric material, in an either aqueous or organic solvent, is applied through spray atomization technique. Moreover, in lesser and less popular cases, coatings are also applied by pouring the same solutions or dispersions which is also called Ladle process [36, 37].

12.3.1.1 Sugar Coating

It is one of the oldest methods of coating and which is still used. Although the major ingredient is sugar (sucrose) for coating which is applied through various steps and coats, the process, however, also needs an initial coating of a hydrophobic material such as shellac, a natural polymeric resin for the sealing phase. Shellac protects the tablets from physical and chemical degradation due to the subsequent coating steps containing aqueous-based sugar solutions. Other materials such as Zein and Cellulose acetate phthalate are used for the same purpose. Major phases in the coating after sealing are subcoating, smoothing, coloring, polishing, and imprinting. The overall method is performed in conventional coating pans by Ladle process; however, the spray coating technique has also gained popularity in the last two decades. Excipients used have wide acceptance with less regulatory issues. The disadvantages attributed to it are more labor skills required as the process is more art than science. During the process, the tablet weight is increased considerably and affects the disintegration time [37].

12.3.1.2 *Film Coating*

Film coating is a procedure whereby a thin film of polymeric substance is applied over the surfaces of dosage forms and drug delivery systems. It is usually accomplished through atomized spraying of solution or dispersion of polymers in an either aqueous or organic solvent. Depending upon the soluble and permeable properties rendered by the coated film onto the surface of the dosage form which is characteristic of the chemical nature and physical properties of the polymer, the film coatings can be broadly classified as soluble, insoluble, gastro-resistant (pH-dependent solubility), and semi-permeable membranes.

12.3.1.3 *Soluble Film Coating*

Soluble film coating is usually applied as a thin film over the dosage form to protect the product from atmospheric oxidation, friability, and render taste-masking properties to the product as well. The thin film coat ensures that the shape of the tablet along with embossing is intact and visible. Various polymeric substances used to coat soluble films are discussed below.

12.3.1.3.1 *Cellulose Ethers*

Cellulose ethers are produced by substituting hydrogen atoms of hydroxyl groups with alkyl groups in anhydrous units of cellulose. These are high molecular weight compounds and their properties depend on molecular weight, chemical structure, substitution group, its degree, and distribution. These properties that are significant for coating include viscosity, solubility, surface activity, thermoplasticity of film, and stability against heat, oxidation, hydrolysis, and biodegradation. Viscosity is directly related to the molecular mass. Most commonly used cellulose ethers (as mentioned in Tables 12.1) for soluble film coatings include hydroxypropylmethylcellulose (HPMC), methylcellulose (MC), hydroxyethylcellulose (HEC), and hydroxypropyl cellulose (HPC) [38].

12.3.1.3.1.1 *METHYLCELLULOSE (MC)*

Methyl ether of cellulose is known as methylcellulose (MC). It is produced by the reaction of methyl chloride and alkaline cellulose. It is made from natural cellulose and is white or milky white in color. It is used as a film-former, emulsifier, adhesive, and thickening agent. However, its use in

Table 12.1 Physical attributes of some commercial soluble and non-soluble coating polymers.

Coating polymer	Other names	Grades	Solubility	Molecular weight	Glass transition temperature (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Hydroxypropyl methyl cellulose	Hypromellose	KAM, K15MP, K100MP, E10MP CR, E4MP, K100LVP, E3PREMLV, E5PREMLV, E6PREMLV, E15PREMLV, E50PREMLV, K3PREMLV	Practically insoluble in ethanol (95%), ether and chloroform. Soluble in water (cold), mixture of dichloromethane with methanol or ethanol and mixture of alcohol with water.	10,000–1500,000	180°C	24–120,000 cP	In oral pharmaceutical formulations like tablets and capsules different viscosity grades are widely used to retard drug release at 10–80% w/w levels.	Hebei Derek Chemical Limited, Kima Chemical (Zibo) Co., Ltd, Sidley Chemical Co. Ltd, etc.	[40, 45]

(Continued)

Table 12.1 Physical attributes of some commercial soluble and non-soluble coating polymers. (Continued)

Coating polymer	Other names	Grades	Solubility	Molecular weight	Glass transition temperature (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Methylcellulose	Methocel	A4MP, A15-1V, A15CP, A4CP	Practically insoluble in water (hot), ethanol, toluene, acetone, saturated salt solutions, chloroform, ether and methanol. Soluble in equal volumes of chloroform and ethanol and glacial acetic acid. It forms a clear to opalescent viscous colloidal dispersion as methylcellulose swells and slowly disperses.	10,000–220,000 Da	184°C –197°C	15–4,000 cP	In tablet formulations may be added to produce sustained release of drug	SE Tylose GmbH & Co. KG, The Dow Chemical Company, etc.	[40]

(Continued)

Table 12.1 Physical attributes of some commercial soluble and non-soluble coating polymers. (Continued)

Coating polymer	Other names	Grades	Solubility	Molecular weight	Glass transition temperature (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Ethylcellulose	Ethocel	EthocelStd 4 Premium N-7, EthocelStd 7PP Premium, EthocelStd 7 Premium N-10, EthocelStd 10FP Premium, EthocelStd 10P Premium N-14, EthocelStd 20P Premium N-22, EthocelStd 45P Premium N-50, N-100 EthocelStd 100FP Premium, EthocelStd 100P	Practically insoluble in water; propylene glycol and glycerin. Freely soluble in mixture of ethanol and hydrocarbons, chloroform, tetrahydrofuran and methyl acetate if ethoxyl group of ethyl cellulose is less than 46.5% whereas greater than 46.5% ethoxyl group of ethyl cellulose show solubility in methanol, toluene, chloroform, ethyl acetate and ethanol (95%).	454.5 g/mol	129°C -133°C	3–110 cP	In oral formulations ethylcellulose is used to coat granules and tablets to modify the drug release.	Sidley Chemical Co. Ltd etc.	[40, 45].

(Continued)

Table 12.1 Physical attributes of some commercial soluble and non-soluble coating polymers. (Continued)

Coating polymer	Other names	Grades	Solubility	Molecular weight	Glass transition temp. (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Hydroxyethyl cellulose	Cellose WP (02), WP and QP (09, 3, 40, 300, 4400), QP (10,000, 15,000, 30,000, 52,000, 100 M) Natrosol HHR, H4R, HR, MHR, MR, KR, GR, ER, JR, LR.	HHR, H4R, HR, MHR, MR, KR, GR, ER, JR, LR.	Hydroxyethylcellulose forms uniform and clear solution in both cold and hot water. Partially solubilize or swell in some polar organic solvents like glycols. Practically insoluble in most organic solvents, toluene, acetone, ether and ethanol.	806.9 g/mol	120°C	Cellosize WP 7–20 cP, WP and QP 10–5,200 cP, QP/50–21,000 cP Natrosol HHR, H4R, HR, MHR 800–5,000 cP, MR, KR, GR, ER 25–6500 cP _s , JR, LR 750–400 cP	Hydroxyethylcellulose is a nonionic, water soluble polymer that is used to form film coats on tablets.	Kima Chemical (Zhbo) Co., Ltd, Sidley Chemical Co Ltd, etc.	[40]

(Continued)

Table 12.1 Physical attributes of some commercial soluble and non-soluble coating polymers. (Continued)

Coating polymer	Other names	Grades	Solubility	Molecular weight	Glass transition temp. (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Hydroxypropyl cellulose	Hypolose, Klucel, Methocel	Klucel HF, Klucel MF, Klucel GF, Klucel JF, Klucel LE, Klucel EF	Soluble in water (1 in 2 parts), methanol (1 in 2 parts), ethanol (1 in 2.5 parts), dichloromethane (1 in 10 parts), propylene glycol (1 in 5 parts), propan-2-ol (1 in 5 parts), Practically insoluble in oils, hydrocarbons, carbon tetrachloride and aromatic hydrocarbons.	50,000–1,250,000	105°C	Klucel HF-EF750–4000 cP.	It is used as a film forming and extended release matrix former agent. It is also used as a binder in tablet dosage form.	Hebei Derek Chemical Limited, Kima Chemical (Zibo) Co., Ltd,	[40, 45]

(Continued)

Table 12.1 Physical attributes of some commercial soluble and non-soluble coating polymers. (*Continued*)

Coating polymer	Other names	Grades	Solubility	Molecular weight	Glass transition temp. (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Polyvinylpyrrolidone	Kollidon, Plaslodone-polyvidone	Povidone K-12, Povidone K-15, Povidone K-17, Povidone K-25, Povidone K-30, Povidone K-60, Povidone K-90, Povidone K-120	Practically soluble in different organic solvents and water.	2,500–3,000,000	168°C	10–20 cP	Povidone solutions may be used as coating agents.	BASF	[40, 45]
Sodium Carboxymethyl Cellulose	Carmellose sodium	Akucell AF (0305,2785,3085)	Practically insoluble in toluene, ethanol, acetone, and ether.	90,000–700,000	135°C	150–12,000 cP	In oral pharmaceutical formulations widely used as a coating agent.	Shanghai Honest ChemCo, Ltd	[40, 46]

film coating is rare, due to unavailability of low viscosity material, as per compendial requirement [37].

A clear solution is formed upon the dissolution of methylcellulose in cold water. However, upon heating, gel is formed. The gelling process is based on flocculation, where molecules lose their water of hydration, and as a result, molecules pack together more closely. These films stretch when pulled; this property is also observed in other cellulose derivatives. A 3% solution of MC produces a film of $\sim 1,000$ μm thickness and have enough strength to peel off in one piece [39].

It is slightly hygroscopic, and the bulk must be stored in a cool dry place in a well-closed container. At room temperature, its solution is stable in alkalis and dilute acids having pH 3–11. Methylcellulose powder is stable, although slightly hygroscopic. At pH lower than 3, it is susceptible to acid-catalyzed hydrolysis. It is also prone to microbial spoilage, and therefore, preservatives should be added to its solution [40].

12.3.1.3.1.2 HYDROXYPROPYLMETHYL CELLULOSE (HPMC)

Hydroxypropyl methylcellulose (HPMC), also known as hypromellose, is a soluble methylcellulose ether. It is used as a binder, thickening agent, film former, and hydrophilic matrix material. Different viscosity grades of HPMC are available for fabricating hydrophilic matrix systems that range from 4,000–100,000 mPa.s as shown in Table 12.2. The use of HPMC for film coating dates back to the initial days of coating [41].

It is mixed alkyl and hydroxyalkyl cellulose ether consisting of methoxy and hydroxypropyl groups. It is synthesized by reacting alkali treated cellulose with methyl chloride in order to add methoxy groups and then with propylene oxide to add propylene glycol ether groups. HPMC is most widely used cellulose ether due to its wide availability, ease of use, enhanced film forming capability, biocompatibility, and biodegradability. It is soluble in both organic solvents and aqueous media used for film coating. Due to its water solubility, the HPMC film can be colored by the use of pigments to get the clear film. Its non-tacky nature makes processing relatively easier. An aqueous solution of 10%–15% w/w low viscosity polymer can be sprayed for forming a film. The film produced by HPMC is strong, but not stronger than methylcellulose [37, 42].

It has linear structure and nonionic nature, which is ideal for micelle formation or for development of the film. The larger hydroxypropyl groups tend to keep polymer chains apart due to steric hindrance. When a 3% HPMC solution is cast, a film of 500 μm thickness is produced. This film is strong and can be peeled in one piece [42].

Table 12.2 Characterization of some film coating polymers related to commercial viscosity grade available.

Coating polymer	Grades	Viscosity
Hydroxypropyl methyl cellulose	K4M, K15MP, K100MP, E4MP, E10MP CR, K100LVP, E3 PREM.LV, E5 PREM.LV, E6 PREM.LV, E15 PREM.LV, E50 PREM.LV, K3 PREM.LV	K100LVP (80–120 cP), K4M (3,000–5,600 cP), K15MP (12,000–21,000 cP), K100MP (80,000–120,000 cP), E4MP (3,500–5,600 cP), E10MP CR (8,000–13,000 cP), E3 PREM.LV (2.4–3.6 cP), E5 PREM.LV (4–6 cP), E6 PREM.LV (5–7 cP), E15 PREM.LV (12–18 cP), E50 PREM.LV (40–60 cP), K3 PREM.LV (2.4–3.6)
Methylcellulose	A4MP, A15-LV, A15CP, A4CP	A4MP (4,000 cP), A15-LV (15 cP), A15CP (1,500 cP), A4CP (400 cP).
Ethylcellulose	Ethocel Std 4 Premium N-7, Ethocel Std 7FP Premium, Ethocel Std 7 Premium N-10, Ethocel Std 10FP Premium, Ethocel Std 10P Premium N-14, Ethocel Std 20P Premium N-22, Ethocel Std 45P Premium N-50, N-100 Ethocel Std 100FP Premium, Ethocel Std 100P	EthocelStd 4 Premium (3–5.5 cP) N-7 (5.6–8 cP), EthocelStd 7FP Premium (6–8 cP), EthocelStd 7 Premium (6–8 cP), N-10 (8–11 cP), EthocelStd 10 FP Premium (9–11 cP), EthocelStd 10 P Premium (9–11 cP), N-14 (12–16 cP), EthocelStd 20P Premium (18–22 cP), N-22 (18–24 cP), EthocelStd 45P Premium (41–49 cP), N-50 (40–52 cP), N-100 (80–105 cP), EthocelStd 100FP Premium (90–110 cP), EthocelStd 100P (90–110 cP)

(Continued)

Table 12.2 Characterization of some film coating polymers related to commercial viscosity grade available. (Continued)

Coating polymer	Grades	Viscosity
Hydroxyethylcellulose	Cellosize (Types and Grades) WP (02), WP and QP (09, 3, 40, 300, 4400), QP (10,000, 15,000, 30,000, 52,000, 100 M) Natrosol HHR, H4R, HR, MHR, MR, KR, GR, ER, JR, LR.	Cellosize WP (02; 5% w/v) 7-20cP , WP and QP (09 - 3; 5% w/v) 60-350 cP; WP and QP (40-4400; 2% w/v) 70-5200 cP; QP(10,000-15,000;2% w/v) 5,700-21,000 cP; (30,000-100 M; 1% w/v) 950-3,000 cP; Natrosol HHR (1% w/v) 3,400-5,000 cP, H4R (1% w/v) 2,600-3,300 cP, HR (1% w/v) 1,500-2,500 cP, MHR (1% w/v) 800-1,500 cP, MR (2% w/v) 4,500-6,500 cP, KR (2% w/v) 1,500-2,500 cP, GR(2% w/v) 150-400 cP, ER (2% w/v) 25-105 cP, JR (5%) 150-400 cP, LR (5%) 75-150 cP.

(Continued)

Table 12.2 Characterization of some film coating polymers related to commercial viscosity grade available. (*Continued*)

Coating polymer	Grades	Viscosity
Hydroxypropyl cellulose	Klucel HF, Klucel ME, Klucel GF, Klucel JF, Klucel LF, Klucel EF	Klucel HF (1%) 1,500–3,000 cP, Klucel MF (2%) 4,000–6,500 cP, Klucel GF (2%) 150–400 cP, Klucel JF (5%) 150–400 cP, Klucel LF (5%) 75–150 cP, Klucel EF (10%) 200–600 cP.
Polyvinylpyrrolidone	Povidone K-12, Povidone K-15, Povidone K-17, Povidone K-25, Povidone K-30, Povidone K-60, Povidone K-90, Povidone K-120	Aqueous viscosity of polyvinylpyrrolidone is expressed as a K-value that ranges from 10 to 20.
Sodium Carboxymethyl Cellulose	Akucell AF (0305; low), (2785; medium), (3085; high)	Akucell AF (0305) 10–15 cP, Akucell AF (2785) 1,500–2,500 cP, (3085) 8,000–12,000 cP.

HPMC solution is stable at pH 3–11. It forms a viscous solution upon dissolution in water with improved enzyme-resistance and higher stability during long-term storage. However, these solutions are susceptible to microbial spoilage and should be preserved with a preservative. The powder form of the material should be stored and kept in a cool and dry place. The common brands available for coating applications of HPMC are Tylopur® (low viscosity Hypromellose), Pharmacoat®, and Tylose® MO (modified HPMC) [40].

12.3.1.3.1.3 HYDROXYETHYL CELLULOSE (HEC)

HEC is water soluble cellulose ether and is insoluble in organic solvents. It is used as a film coating agent, binder, controlled release matrix former, viscosity modifier, suspending agent and thickening agent in topical and ophthalmic preparations. It is mentioned in US-NF and there is no specific requirement for the presence of hydroxyethyl group. The pharmacopeia also allows the presence of additives to enhance powder dispersion in water and to avoid caking on storage [37].

HEC is highly hygroscopic and therefore should be stored in a tightly closed container at cool and dry place. It is tasteless, odorless grayish-white, yellowish-white, or white color hygroscopic powder. The aqueous solutions of hydroxyethyl cellulose are stable in the range from pH 2–12 and viscosity are also unaffected [43]. Although below pH 5 there are chances of hydrolysis and at high pH, oxidation may occur. Increase in temperature may lead to a reduction in viscosity. However, it is restored on cooling. It is susceptible to enzymatic degradation by bacteria and fungi present in the atmosphere. Thus, antimicrobial agents must be added to its aqueous solution. Available brands for HEC for coating applications include Natrosol®, Tylose® H, Tylose® HS, and Tylose® CER [40].

12.3.1.3.1.4 HYDROXYPROPYL CELLULOSE (HPC)

Hydroxypropyl cellulose (HPC) is a water-soluble, non-ionic, hygroscopic polymer that is used for film coatings, binder, and controlled release matrix. Furthermore, it has also been used as a viscosity enhancer, suspending agent, stabilizing agent, thickening agent, and emulsifying agent. It is prepared by partial or complete substitution of the hydroxyl group on the glucose unit of cellulose by hydroxypropyl groups. The viscosity of polymer depends upon the degree of polymerization [44]. It is soluble in the both aqueous and alcoholic medium. Its film appears to be tacky, that makes the film weak and resists rapid coating. In order to increase adhesion to the substrate, it is used with other polymers [37].

It is stable material but become hygroscopic after drying, thus for appropriate storage, it is required to be kept at an ambient conditions with low moisture content in a tightly closed container. Its aqueous solution is stable at pH 6–8. At low pH, the solution undergoes acid hydrolysis also leading to decrease in viscosity. At high pH, oxidation may occur, leading to polymer degradation and loss of viscosity [40]. Coating application brands of HPC are available as Klucel® (Ashland) and Celny®.

12.3.1.3.1.5 CARBOXYMETHYL CELLULOSE (CMC AND NA-CMC)

Carboxymethylcellulose (CMC) is a polyelectrolyte polymer with anionic character. It is also available in the form of sodium salt (Na-CMC). It is carboxy methylether derivative of cellulose achieved through the semi-synthetic process. Common names employed are Carmellose Sodium, Carmellosum Natricum, Cellulose gum, Cethylose, Carbose D. Various brands of Na-CMC are available including Akucell®, Aqualon®, Aquasorb®, Blanose®, Walocel® C, Finnfix® Tylose® CB; Tylose® MGA. Na-CMC is a tasteless, odorless, white granular powder that becomes hygroscopic after drying. It is soluble in water (hot and cold) and forms mucilage due to the presence of the polar carboxyl group. CMC is used as film forming agent, viscosity enhancer, binding, suspending, thickening, stabilizing agents, disintegrant, and water-absorbing agent [40, 43].

12.3.1.3.2 Polymethacrylates

Poly(methacrylic acid) was the first methacrylate polymer introduced in 1880. Poly(methyl methacrylate) (PMMA) was developed 48 years later. It was marketed in 1993 and is most widely used methacrylate polymer. The worldwide production of methacrylate polymers exceeds two million metric tons annually [38].

Chemically, polymethacrylates are ionic (anionic and cationic) synthetic polymers of methacrylic acid, its esters (varying ratios), and dimethylamino ethyl methacrylates. They are non-irritant and non-toxic polymers and are mostly used for film coating applications on tablets [40].

Polymethacrylates can be classified as pH-independent and pH-dependent polymers. pH-independent polymers are used for extended-release formulations, while pH-dependent polymers are used for enteric coatings; these are a methacrylic acid copolymer, which is soluble at the pH range of proximal to distal intestine. The Eudragit E with amino functional groups tends to exhibit pH-independent solubility in the gastrointestinal pH range. The other grades of polymethacrylates marketed are discussed in the proceeding section of gastro-resistant coatings [40, 43].

12.3.1.3.3 Polyvinyl Derivatives

12.3.1.3.3.1 POLYVINYL ALCOHOL (PVA)

Polyvinyl alcohol is a hydrophilic polymeric material with high aqueous solubility. It has chemical empirical formula of $(C_2H_4O)_n$, where n varies between 500–5,000. The commercially available grades of polyvinyl alcohol have molecular weight in the range of 20,000–200,000 $gmol^{-1}$. It is primarily a hydrolytic product of polyvinyl acetate and the physicochemical properties are thus dependent on the degree of hydrolysis and polymerization. It has also been used as a coating agent, viscosity increasing agent, stabilizing agent, lubricant, and for the preparation of sustained release formulations [40, 43].

12.3.1.3.3.2 POLYVINYLPIRROLIDONE (PVP)

Polyvinylpyrrolidone, chemically expressed by formula $(C_6H_9NO)_n$, is a non-ionic synthetic hydrophilic polymer having high hygroscopicity and excellent water solubility. It also has high solubility in chlorinated (e.g., dichloromethane and chloroform) and alcoholic (e.g., ethanol) solvents. Common names employed for PVP are polyvidone, povidonum, E1201, Povipharm, 1-vinyl-2-pyrrolidinone, and poly[1-(2-oxo-1-pyrrolidinyl) ethylene] polymer. The marketed brands for PVP are Plasdone® (Ashland) and Kollidon® (BASF). The molecular weights of commercially available brands range from 2,500 to 3,000,000 $gmol^{-1}$. Its aqueous viscosity (K-value) ranges from 10 to 120 as mentioned in Table 12.2. It is used as dissolution enhancer, binder, disintegrant, suspending agent. Since it has high Hygroscopicity, it is recommended to use it with other suitable insoluble polymeric agents for coating of granules and tablets [40, 43].

12.3.1.3.3.3 POLYVINYLPIRROLIDONE-VINYL ACETATE COPOLYMER (COPOLYMER (COPOVIDONE))

Polyvinylpyrrolidone-vinyl acetate copolymer is commonly known as Copolyvidone, PVP/VA copolymer, poly(1-vinylpyrrolidone-co-vinyl acetate), polymer with 1-vinyl-2-pyrrolidinone, acetic acid vinyl ester, acetic acid ethenyl ester, 2:3 ratio copolymer of vinyl acetate and 1-vinyl-2-pyrrolidone, and 2:3 copolymer of ethenyl acetate and 1-ethenylpyrrolidin-2-one. The brands available are Plasdone® S-630, Luviskol® VA (BASF), Kollidon® VA 64 (BASF). It is used as a film forming agent, binder, and granulation aid [40, 43].

12.3.1.4 *Insoluble Film Coating*

12.3.1.4.1 Ethylcellulose (EC)

Ethylcellulose is a water-insoluble, non-irritant, non-allergenic, and non-toxic polymer which is primarily used to modify drug release by applying hydrophobic coats. It is composed of β -anhydroglucose monomeric units with interlinking acetal bonds. Ethylcellulose powder is white to light tan-color, free flowing, and tasteless. This polymer is widely used as a tablet coating material and also sometimes used as tablet binder and viscosity enhancing agent while rarely used as a tablet filler and flavoring agent [43]. The available brands of ethylcellulose (EC) are Aquacoat® ECT (30% latex dispersion of EC) and Surelease® (30% colloidal dispersion in aqueous aluminum hydroxide). Both of these brands also contain additives in various proportions to support the elastic formation of the film on drug products [40].

12.3.1.5 *Gastro-Resistant Film Coating*

The gastro-resistant coating was first reported by Unna in 1884. It is the most established technology of all modified released drug delivery systems. Acid sensitive and gastric irritant drug products are commonly coated with gastro-resistant polymeric materials which ultimately prevent the release of such molecules in the gastric cavity. It is achieved by the coating of the delivery system with weakly acidic polymer, consisting of carboxylic acid group, which remain intact in the acidic environment while dissolves near neutral pH. Shellac, gelatin, and keratin were initially used to fulfill this purpose. Over time, various synthesized polymers (as mentioned in Table 12.3) were available in the market to play this role [47]. Commonly used polymers for enteric coating include cellulose acetate phthalate (CAP), polyvinyl acetate phthalate (PVAP), and hydroxypropyl methylcellulose phthalate (HPMCP) and poly-methacrylates [47].

12.3.1.5.1 Shellac

Since 1930, shellac has been frequently used alone or in combination with other materials as an enteric coating polymer. Wruble investigated the use of various solutions for enteric coating and concluded that the shellac ammonia solutions were the best among all. However, due to numerous reported disadvantages, it is no longer used for this purpose. Being of natural origin, the material may vary from batch to batch. Its tackiness also

Table 12.3 Physical attributes of some commercial gastro-resistant polymers.

Coating polymer	Other names	Type	Solubility	Molecular weight	Glass transition temp. (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Hydroxy-propyl-methyl-cellulose phthalate	Hypromellose Phthalate, Hydroxy-propylmethyl-cellulosephthalat	Organic (Cellulose ether)	Soluble at pH greater than 4.2 while at low pH show limited solubility	240.30 g/mol	129.6°C -130.7°C	320–480 cP	Enteric coating agent for tablet and granules: 5–10% soluble in solvent mixture of dichloromethane (50): ethanol (50) and water (20) : ethanol (80)	Sigma-Aldrich, Career henan chemical co, Henan DaKen Chemical Co., LTD, Etc.	[40, 42]
Cellulose acetate phthalate	Aquacoat CPD; CAP; Cellacefat; cellulose acetate benzene-1,2-dicarboxylate	Organic (Cellulose acetate)	Practically insoluble in water and alcohols. It is soluble in certain buffered aqueous solutions (pH ≥ 6.0)	3921.085 g/mol	160°C –170°C	500–900 cP	Enteric film coating, matrix binder in pharmaceuticals	Sigma-Aldrich, Henan DaKen Chemical CO.,LTD, Henan Tianfu Chemical Co.,Ltd.	[40, 42]

(Continued)

Table 12.3 Physical attributes of some commercial gastro-resistant polymers. (Continued)

Coating polymer	Other names	Type	Solubility	Molecular weight	Glass transition temp. (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Polyvinyl acetate phthalate	Phthalavin; PVAP; Opaseal; Sureteric	Organic (vinyl acetate polymer)	Practically insoluble in water but soluble in methanol and ethanol. Sparingly soluble in propan-2-ol and acetone. Polyvinylacetate phthalate(200mg/L) shows pH dependent solubility in buffer solutions, i.e., below pH 5 insoluble and above pH 5 soluble. Ionic strength also influences solubility.	60,700 g/mol	23.5°C–42.5°C	75–110 cP	Used as enteric film coating agent in 9%–10% and sealant in tablet sugar coating in 28%–29%	Colorcon (Opadry-Enteric), Hubei Jusheng Technology Co., Ltd.S.Z. PhyStandard Bio-Tech. Co., Ltd.	[40, 42]

(Continued)

Table 12.3 Physical attributes of some commercial gastro-resistant polymers. (Continued)

Coating polymer	Other names	Type	Solubility	Molecular weight	Glass transition temp. (Tg)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Polymethacrylates	Acryl-EZE; Eudragit (E, L, S, FS, RL, RS); Kollicoat MAE, Eastacryl 30D	Acrylic-based polymers	Acetone and Alcohol	150,000–800,000 g/mol	45°C–150°C	Eudragit E3–1.2 cP, Eudragit NE 30 D (450 cP), Eudragit L and S (50–200 cP), Eudragit FS 30 D (420 cP), Eudragit L 30 D-55 (415 cP), Eudragit L 100-55 cP, Eudragit (100–200 cP), Eudragit RL and RS (415 cP), Eudragit RL and RS 30 D (42,000 cP), Kollicoat MAE and Kollicoat MAE 100 P 30 DP (415 cP), Eastacryl 30D (145 cP)	Eudragit E (film-forming agent) and Eudragit L 30 D-55, S & FS, East acryl 30 D and Kollicoat MAE 30 DP (enteric coating agent)	Evonik (Eudragit E, L, S, FS, RL, RS); (Acryl-EZE®), Acryl-EZE® II, Opadry® Enteric, Sureteric®BASF (Kollicoat), etc.	[40, 59]

(Continued)

Table 12.3 Physical attributes of some commercial gastro-resistant polymers. (*Continued*)

Coating polymer	Other names	Type	Solubility	Molecular weight	Glass transition temp. (T _g)	Viscosity	Pharmaceutical application	Manufacturer	Reference
Hydroxypropyl methyl cellulose Phthalate	Hypromellose Phthalate, Cellulose phthalate hydroxypropyl methyl ether, HP-50, HP-55	Semi synthetic Organic (cellulose-Phthalate derivative)	Ethanol/Water mass ratio 80/20, methylene, chloride/ethanol ratio 60/40, mixture of dichloro-methane and methyl alcohol (1:1), ethyl or methyl alcohol and acetone (1:1)	80,000–130,000 g/mol	133°C–137 °C	HP-55: 320–480 cP; HP-50: 440–560 cP	12%–15% as enteric coating agent.	Colorcon (Opadry Enteric), Shin-Etsu Chemical Co. Ltd;	[40, 60–62]

makes it difficult to apply as a coating material. Delivery systems coated with shellac, which is stored for 12 months failed to disintegrate at intestinal pH. This occurs due to the polymerization of shellac. Since most of the enteric coated formulations tend to dissolve between pH 3.8 to 6.9, the failure of shellac to dissolve below pH 7 is a major drawback [48].

Shellac resin comprises esters of shellolic acids and aleuritic, which impart the enteric coating characteristics of the material. The precise composition of shellac may differ depending on the source of the polymeric substance and/or manufacturing process. According to NF, four types of shellac are listed based on the method of preparation [49]. It is usually applied as an alcoholic solution or aqueous dispersion. Although shellac possesses various disadvantages and is not preferred to be used as an enteric coating polymer, its use with slight modification in terms of its functionality and to increase its stability has been extensively reported in the literature [50].

12.3.1.5.2 Cellulose Acetate Phthalate (CAP)

Cellulose acetate phthalate is one of the most popular and oldest synthetic polymer for gastro-resistant coating introduced and patented in 1940 by Eastman Kodak. It is a mixed cellulose ester, wherein esterification of one carboxyl group of phthalic acid occurs due to reaction with the hydroxyl group of cellulose. It is a white powder with high flowability and a slightly acetic acid odor. As per the requirements of JP, the acetyl and phthalyl content must be 17%–22% and 30%–40%, respectively, while the USNF requirements are 21.5%–26% and 30%–36%, respectively. As it is prone to hydrolysis, the pharmacopeias specify the maximum limits of loss on drying and quantity of free acid [51, 52].

It is a polymeric acid and ionizes and dissolves in the high pH region of the gastrointestinal tract. However, literature also suggests that dissolution of CAP is attributed to the hydrolytic action of intestinal esterases rather than ionization. It is also permeable to water vapor, ionic substances, and gastric fluid. The permeability depends on numerous factors such as type and quantity of plasticizer and the presence or absence of other solid materials [48].

CAP stability is not affected if it is kept in a closed container at a cool and dry place. However, at high temperature and humidity, slow hydrolysis may occur leading to an increase in its viscosity, free acid content, and acetic acid odor [40].

Cellulose acetate phthalate is commonly used to coat oral enteric delivery systems such as tablets and granules. Beside various companies offering various grades of CAP, Aqua Coat® CPD is the most recognized product of CAP for coating applications.

12.3.1.5.3 Polyvinyl Acetate Phthalate (PVAP)

Polyvinyl acetate phthalate is another commonly used polymer for gastro-resistant coating applications that was introduced and patented by a Canadian company, Charles E. Frost, and later, it was further studied by Millar in 1957, who characterized the impact of the polymer's phthalyl content on the pH of tablet disintegration medium. The optimal content of phthalyl was found to be between 60% and 70%. Though, currently, this range has been revised for commercially available polymers, and has become part of the USP-NF monograph. It is prepared by random synthesis of polyvinyl alcohol with phthalic anhydride and acetic acid [51].

Like other polymers containing phthalate, its aqueous solubility is pH dependent, i.e., at low pH, it is insoluble though quickly dissolves at pH 5. It is less permeable to simulated gastric fluid and water vapors than CAP and other polymers of the same class. This property makes it a good enteric polymer. Like other phthalate containing polymers, it is prone to hydrolysis; however, it is more stable as compare to HPMCP and CAP [48].

12.3.1.5.4 Hydroxypropyl Methylcellulose Phthalate (HPMCP)

Hydroxypropyl methylcellulose phthalate (HPMCP) is a derivative of cellulose in which hydroxyl groups are substituted by 2-hydroxypropyl ethers, methyl ethers, or phthalyl esters. It was introduced in 1971 as an enteric coating polymer. Common names employed for HPMCP are hydroxypropyl methylcellulose benzene-1,2-dicarboxylate, cellulose phthalate hydroxypropyl methyl ether, methylhydroxypropylcellulose phthalate, 2-hydroxypropyl methyl cellulose phthalate, Hypromellose phthalate, HP-5, and HP-55 [53, 54].

It is a white powder or granular substances. USP and JP monographs describe two types of substitution, i.e., HPMCP 220824 and HPMCP 20073. The specification denotes to the percentage substituent of respective methoxyl, hydroxypropyl, and carboxybenzoyl groups [51].

HPMCP like other phthalate containing enteric coating polymers is insoluble in water and gastric medium but ionizes and dissolves in the upper small intestine where pH increases. The numerical descriptions that follow letter HP indicate the pH at which it dissolves. For, e.g., HP-55 hydrates and dissolves at pH 5.5. HPMCP disintegrates and releases more rapidly in the intestine as compared to other polymers. However, it could also release in the stomach of some individuals in the fed state [48].

It is physically and chemically stable for 3–4 years at ambient temperature and for 2–3 months at stress condition (40°C and 75% relative humidity). It is not susceptible to microbial degradation at ambient storage

conditions and generally more stable than cellulose acetate phthalate. HPMCP is extensively used in the development of various conventional and advanced gastro-resistant drug delivery systems [55].

12.3.1.5.5 Polymethacrylates

Polymethacrylates are synthetic polymers with anionic and cationic characteristics. They are synthesized products of methacrylic acid, methacrylic acid esters, and dimethyl aminoethyl methacrylates in different ratios [56]. These polymers are marketed by Evonik Industries commonly denoted as Eudragit®. They can be classified as pH independent and pH dependent polymers as discussed earlier. Polymers such as Eudragit L 30 D-55 / L 100-55 and Eudragit L 100 have a high content of carboxylic acid groups and are soluble at low pH of proximal intestine. Hydrophobic polymers such as Eudragit S 100 and Eudragit FS 30 D dissolve at higher pH and are used for colonic drug delivery systems [57, 58].

The use of plasticizers is recommended along with the polymers. Due to the sticky nature of the polymers, it is also suggested to add pigments and opacifier. These polymers can bind to the large quantity of pigments, approximately 2–3 times of polymer used. In order to improve the gloss of the final product, polyethylene glycols are commonly used.

Eudragit S100 and L100 are commercially available in powder form and concentrates in an organic solvent, which can be further diluted for processing. These polymers comply with US-NF requirements [51].

Dry powders of polymethacrylates are stable for 3 years when stored below 30°C in a well-closed container. Above this temperature, clumps are formed, which can be easily broken. Although, it doesn't affect the quality of the product. Dispersions of polymethacrylates are stable for 18 months when stored between 5°C–25°C in a tightly closed container. Phase separation may occur in dispersions below 8°C [40].

12.3.1.6 Semi-Permeable Film Coating

Osmotic drug delivery devices offer a zero-order drug release pattern, which is almost independent of the pH, food, and other hydrodynamic conditions of gastro intestinal tract. Rose-Nelson osmotic pump is considered as the first drug delivery system working on the principle of osmosis [63]. In early 1970s, ALZA Corporation proposed several variations in Rose-Nelson pump and was first to design an oral osmotic drug delivery system that was called as OROS. In the current era, numerous medicinal products are designed by OROS technology [64].

The rate controlling membrane (film coated semi-permeable membrane) plays a significant role in the design of an osmotic system and impart selective permeability character for water molecules against the drugs and other ingredients existing in the device core like osmotic agents. These film coated membranes are required to possess adequate water permeability and enough strength to bear the pressure within the device and maintain its physical stability during the life span of the system. The thickness of membrane is typically kept in between 0.2 mm and 0.3 mm. The membrane should be inert, firm, and non-swelling [64–66]. The drug release rate and thickness of semi-permeable membrane have an inverse relation. As the thickness of the semi-permeable membrane increases the resistance to water diffusion also increases and hence drug release rate decreases. Generally, 1/1000 to 50/1000 portions of a plasticizer are used alone or with coating substances [65–67].

There are many polymers that are a constituent part of coating recipes that can be used to create semi-permeable membrane for osmotic DDS. Commonly utilized polymers for coating of tablet cores in osmotic systems are cellulose (C) esters such as cellulose acetate (mono, di, and tri) and cellulose acetate butyrate and cellulose propionate, etc. Moreover, cellulose ethers such as ethyl cellulose (EC) and certain products of Eudragits are also utilized for the purpose.

12.3.1.6.1 Cellulose Acetate (CA)

Cellulose acetate is an acetyl substituted derivative of cellulose polymer and is widely used for semi-permeable coating applications. It is hygroscopic, white free flowing powder with acetyl substitution in the range of 32% to 39.5%. Though other derivatives such as cellulose di and triacetate are also termed as cellulose acetates, they differ in hydroxyl group substitution range and thus imparting different solubility character. CA is generally used to create membranes that control the rate of water influx for osmotic devices. CA membranes are not soluble, yet semi-permeable for water molecules to penetrate them. Water permeability of CA film is adequately achievable and can be easily rectified by differentiating the degrees of acetylation from 32% to 38%. Water permeability characteristic of CA film declines as the acetyl content in CA rises. Absorption of water through the membrane is also augmented by incorporation of hydrophilic natured flux and permeation enhancers. It has been reported that the inclusion of plasticizers in cellulose acetate for coating application on tablet formulations usually reduces the glass transition temperature, increase in the

polymer-chain movement augments the elasticity, and alters the permeation capability of the membrane [66].

12.3.1.6.2 Cellulose Acetate Butyrate (CAB)

Cellulose acetate butyrate also called as cellaburate is produced from reacting acetic anhydride, acetic acid, and cellulose fibers. It is also hygroscopic, white to yellowish-white free flowing powder. CAB is also a semi-permeable polymer and has been used for controlling the release of drugs. It has been found as a commercial alternative to CA for thinner semi-permeable coating applications with increased robustness and decreased drying times [68].

12.3.1.7 *Mucoadhesive Coating Polymers*

Mucoadhesive polymers are a class of natural and synthetic polymers which are coated on dosage forms with a target to adhere to gastric mucosa (mucin) and thereby increasing the residence time in the given part of the gastrointestinal tract. Moreover, they are also known to deliver larger payload of drug to be absorbed directly from the mucosal lining [69]. Most of the cellulose derivatives discussed above are used for this purpose especially for designing multi-particulate gastro-retentive drug delivery systems [70]. Beside cellulose esters and derivative, there are certain other polymeric materials which have gained enormous popularity for this particular role.

12.3.1.7.1 Chitosan

Chitosan is a deacetylated product of chitin, an inelastic mucopolysaccharide. It is creamy-white or white odorless flakes or powder, may look cottonlike as fiber formation occurs during precipitation. Chitosan polymers are commercially available with different molecular weights ranging from 50,000 to 2,000,000 gmol^{-1} . Moreover, grades with varying degrees of deacetylation (40%–98%) and viscosities are also available. It is used as a tablet film forming agent, disintegrant, mucoadhesive coating. It is also used as viscosity enhancing material and binder [40, 43].

12.3.1.7.2 Poly(Ethylene Oxide)

Polyethylene oxide (PEO), a non-ionic homopolymer, is prepared from polymerization of ethylene oxide using a catalyst. It is represented by a chemical formula $(\text{CH}_2\text{CH}_2\text{O})_n$ where n is the average number of oxyethylene groups. Synonyms for PEO are polyoxyethylene, polyoxirane, and

polyoxiante that are available under the brands Polyox® (Colorcon). PEO is off-white to white powder with good flowability and have a slight ammonia like odor. It is soluble in both water and organic solvents like methylene chloride, acetonitrile, and chloroform. It is rapidly eliminated from the body thus showing low levels of toxicity. It is used as a coating agent, mucoadhesive, thickening agent, binder, and for the preparation of immediate and sustained release formulations depending upon the molecular weight [40, 43].

12.3.1.7.3 Poly(Ethylene Glycol)

Polyethylene glycol (PEG) is a non-toxic, non-immunogenic polyether diol, having a general formula $\text{HOCH}_2(\text{CH}_2\text{O CH}_2)_m\text{-CH}_2\text{OH}$ where m is the average number of oxyethylene group. It is a polymerized product of ethylene oxide with common names used as Macrogols, Lipoxol, and Pluriol E. Common brands available for PEG are Carbowax® (Dow Chemical Company), Lutrol® E (BASF), and Carbowax Sentry® (polyethylene glycol and methoxy polyethylene glycol MPEGs). It is mainly used for the preparation of solid dosage form and parenteral due to its combined elimination from hepatic and renal pathways. Being an amphiphilic polymer, it is soluble in both water and organic solvents. The molecular weight ranges from 500 to 20,000 g mol^{-1} . In liquid formulations like oral solutions, solid dispersions, and injections, it increases the solubility of poorly soluble drugs. It prevents bacterial surface growth and deposition of proteinaceous material and thereby is widely used as “Stealth” polymer to ensure long circulation of nanoparticles inside the bloodstream [40, 43].

12.3.2 Solvent-Less Coating Procedures

12.3.2.1 Compression Coating

It is one of the oldest type of dry coating or press coating technique which is characterized as solvent-free method. It is a two-step method, where after compression of the tablet core, coating material is compressed around the core. Procedure needs proper placing of the core tablets on the outer layer forming material as variation in the coating is usually observed if the core is not properly placed at the center [71]. Drug release can be effectively controlled after applying the rate controlling hydrophilic membrane around the core surface. Cellulose-based derivative such as hydroxyethylcellulose (HEC), hydroxypropylmethylcellulose (HPMC), hydroxypropylcellulose (HPC), and carboxymethylcellulose (CMC) are commonly used because of its water solubility and gel forming nature [24]. HEC was used for developing

delayed release system while non-cellulose polymers such as alginate-chitosan complex for time controlled drug delivery, polyethylene oxide (PEO) and polyethylene glycol (PEG) for controlling the lag time before release [72–75]. Compression coating was also used as a taste masking agent for clinical studies was also reported by Hadfield *et al.* in 1987 [76].

12.3.2.2 Hot Melt Coating

Hot melt coating procedure was used for taste masking, stability for controlling the drug release. The coating material is applied in the molten state which was then solidified on cooling [77]. Drug releases mechanism either diffusion or dialysis, enzymatic breakdown or pH dependent dissolution. The coating material beside waxes such as beeswax and carnuba wax or some oils, versatile polymers such as Gelucires with different melting points and polyethylene glycols are also used. Four-step process of coating that begins with the warming of equipment, preheating of the substrate, melting and spreading of the coating material and congealing [23, 77, 78].

12.3.2.3 Dry Powder Coating

Many polymers such as HPMCAS, Eudragit® RSPO, and Eudragit® RLPO were effectively used in dry powder coating where the film forming polymers and plasticizer are separately fed either in a tablet coating pan or fluid bed coater. Powder forms several layers of coating which may be stabilized by spraying a small amount of water during annealing. Refined dry coating process reported by Cerea *et al.* in 2004 where no water even in small quantity is required. Theophylline tablets were coated using Eudragit E PO for coating theophylline tablets [79–81].

12.3.2.4 Electrostatic Spray Powder Coating

This technique was first introduced in USA in the 1950s and now extensively used in different industries for coating due to its distinct advantages such as low operational cost, short processing time, and highly valued for energy savings. In this coating, dry powders are charged by an electrostatic spray gun and sprayed on the surface of the grounded substrate with electrostatic attractions and mechanical forces to form a deposited powder layer. The thickness of each coated layer is controlled by generating an electrical charge which hinders further layering. This deposited

substrate is cured for film formation in an oven at high temperature for a certain period of time. This technique significantly enhances the coating efficiency by increasing the adhesion of coating powder and yields more uniform coating in terms of coating thickness and surface morphology by controlling the feeding of coating powder [82, 83].

12.3.2.5 Supercritical Fluid-Based Coating

The supercritical fluid-based coating is used to coat small particles uniformly under a supercritical condition. The physical and thermal properties of supercritical fluids fall in between pure liquids and gases because their temperature and pressure are greater than their critical temperature (T_c) and pressure (P_c). For pharmaceutical purposes, Carbon dioxide is an ideal supercritical fluid having low critical pressure (72 bar) and temperature (31.1°C). It is non-toxic, inexpensive, easily available, nonflammable, environment-friendly, and can be recycled easily but in the absence of cosolvents, its use is limited for coating. The limitation for this method is that the supercritical fluid dissolves coating material only while leaves the core undissolved. The rapid expansion of supercritical solutions (RESS) is a commonly used process in pharmaceutical industry. The active ingredients are dispersed in a high pressure vessel containing supercritical solution of the coating agent. The solvent power of supercritical liquid is reduced on the rapid expansion of suspension resulting in the precipitation of coating material on to the dispersed drug particles. Cosolvents like acetone and methanol are used to increase the solubility of the compound in supercritical fluid [83, 84].

12.3.2.6 Photocurable Coating

Photocuring coating is the only chemical technique for the formation of coating films but its application is limited to the photocurable materials. The cross-linked network is rapidly formed by the free-radical polymerization reaction of photocurable materials at room temperature or below. This method is not suitable for photosensitive drugs [83].

12.3.3 Polymer Coatings for Micro/Nano Particulate Drug Delivery Systems (DDS)

Nano/microparticulate drug delivery systems are a class of novel drug delivery platforms which are designed to achieve targeted drug delivery

in vivo through various routes of administrations. Although the coating of polymers has been a long discussed topic of conventional dosage forms either to enhance the appearance and increasing the stability of the product or to render functional characteristics to such systems as discussed earlier. Coating of polymeric materials on smart novel drug delivery systems offer various constituent properties to systems and/or at various instances, offer functional characteristics to the particulate drug delivery platforms which may include “stealth coating” of nanoparticles for long circulation and plasma half-life, and conjugating targeting ligands (antibodies, receptor binders) for targeted delivery is the drug payload [85].

12.3.3.1 *Types of Polymer Coating Systems for Specialized DDS*

In case of micro/nanoparticulate drug delivery systems, coating of polymeric materials around the core are either achieved during the fabrication step of the particulate system or after fabrication stage. The major coating techniques on micro/nanoparticulate systems are briefly discussed here.

12.3.3.1.1 Self-Organized/Assembled Coating

Amphiphilic polymeric materials such as block co-polymers consisting of a hydrophilic block and a hydrophobic block are used to prepare a polymeric radial core-shell architecture called micelles. The core of the micelle substance is constituted of drug substance with a shell of radially arranged short amphiphilic polymeric chains. This is usually achieved by dispersing block polymeric substance in an organic drug solution followed by dialysis and then forming an oil/water emulsion where the drug is consolidated into the organic phase and the hydrophobic ends of the polymers face the drug. This is followed by solvent evaporation and freeze drying so that this ensures that aqueous component of the system stays till last and is removed in a solid state so that the hydrophilic ends are exposed towards the exterior. Commonly used polymeric substances for micelle formation are poly(ethylene-glycol)-*b*-poly(L-lysine) (PEG-*b*-PLL), poly(ethylene-oxide)-*b*-poly(propylene-oxide)-*b*-poly(ethylene-oxide) (PEO-*b*-PPO-*b*-PEO), poly(ethylene-glycol)-*b*-poly(aspartic-acid) (PEG-*b*-PAA), etc. Moreover, certain block copolymers such as poly(ethylene-glycol)-*b*-poly(ethylene-imine) (PEG-*b*-PEI) and poly(ethylene-glycol)-*b*-poly(dimethylaminoethyl-methacrylate) (PEG-*b*-PAMA), etc., are also used for the synthesis of gold nanoparticles with micellar core-shell architecture [86–88].

12.3.3.1.2 Coating by Coprecipitation

Coprecipitation technique is a form of micro/nanoparticles synthetic procedure which yields particles with core-shell architecture. The shell, in this case, is composed of polymeric material and the core consists of the drug substance alone or dispersed in a matrix. The process involves the dispersion of a solution of film-forming polymer and drug substance in an organic phase into a non-solvent phase consisting of surfactants in a controlled fashion. This results in the precipitation of polymeric substance encapsulating drug substance as the organic phase is diffused out into the bulk. The three key stages in coprecipitation are (1) nucleation, (2) growth, and (3) aggregation. The process is controlled in a way so as to achieve a uniform sized particle by avoiding excessive aggregation of the particles. The commonly demonstrated polymers for coprecipitation include poly(caprolactone) (PCL), poly(lactide (PLA)), poly(lactide-co-glycolide) (PLGA), and poly(alkylcyanoacrylate) (PACA) [88, 89].

12.3.3.1.3 Coating by Adsorption

Polymeric materials can be coated on micro/nanoparticulate systems by applying coats of polymers through adsorption technique. This is achieved by the adsorption of dissolved or dispersed polymer on the surface of pre-formed particulate matter. The polymers, in this case, possess certain partial charges and are usually dispersed in the aqueous phase. Consequently, they are precipitated onto the surface of the particulate matter; finally, the dispersion medium is evaporated to further precipitate the polymer on the surfaces. The polymers which have been demonstrated for coating by this technique include poly(methacrylate) (PMA), poly(methyl methacrylate) (PMMA), and poly(caprolactone) (PCL) [89].

12.3.3.1.4 Coating through Layer-by-Layer (LbL) Assembly

Layer-by-layer assembly is a simple yet versatile technique used to coat multiple layers of differently charged polymers on the surfaces of micro/nanoparticulate systems. The method involves immersing core material of particulate matter consisting of macromolecules or macromolecular dispersion of drug substance in a solution of differently charged polymer followed by incubation and washing. Subsequently, the particulate matter is again immersed and incubated in another polymer with opposite charge. Thus, by repeating this procedure, multiple layers of polyelectrolyte polymers can be achieved. The cationic polymers which have been demonstrated for LbL assembly include chitosan, poly(ethylene-imine) (PEI) poly(allylamine

hydrochloride) (PAH), poly(dimethyldiallylamide ammonium chloride) (PDDA), similarly anionic polymer used in conjunction include poly(styrene sulphonate) (PSS), carrageenan, poly(vinylpyrrolidone) (PVP), etc. [88, 90].

12.4 Mechanism of Drug Release through Coating Systems

12.4.1 Diffusion

In diffusion-controlled drug delivery system the polymer is employed as a barrier to drug transfer and thereby controls the rate of drug release. From different types of polymethacrylates, polyalkylacrylates have shown diffusion controlled drug delivery. Diffusion controlled systems can be classified into two types: reservoir devices (polymer in form of a membrane is coated over the drug) and matrix devices (dispersed drug in a polymer matrix).

In case of coated reservoir devices, the drug core is generally enclosed by hydrophobic polymeric material and through the mesh (the space between macromolecular chains) of these polymers the drug liberates out. The release rate of drug from a reservoir device is governed by the simplified form of Fick's first law of diffusion, as given below:

$$J = \frac{DK\Delta C}{d}$$

Equation 12.1. Equation for Fick's first law of diffusion

Where, " J " is the rate of drug transfer across a unit plane area, " D " is the diffusion coefficient of the drug in the polymer, " K " is the partition coefficient, " ΔC " is concentration gradient across the polymer membrane and " d " is the thickness of the diffusion layer [91].

12.4.2 Dissolution

Dissolution-controlled systems can be categorized as reservoir type and matrix systems. In case of reservoir systems, hydrophilic polymeric substances form a sheath or membranous layer around drug particles. The liberation rate of drug can be controlled by type of the polymer used for the membrane and its thickness. The formulations containing polymers like carboxymethyl cellulose, gelatin, hydroxyl propylmethyl cellulose, starch, and polyvinylpyrrolidone have been found to show dissolution dependent drug release [92].

12.4.3 Erosion

The release of the drug from biodegradable polymers such as polyglycolic acid, poly lactic-co-glycolic acid, and poly anhydrides, etc., is usually dependent upon the rate of erosion of the polymeric substance that encases the drug particles. The drug is usually trapped in the polymeric matrix system by physical means or on the other hand, the drug could also be chemically bonded to the polymeric structure. In this case, the release of the drug would take place by the chemical bond degradation between polymer and the drug. The mass erosion pattern relay on the aqueous solubility of the polymer. If the polymer is hydrophobic, then the diffusion of water into the matrix will be limited, restricting the polymer erosion to the surface only. In the case of a hydrophilic polymer, erosion takes place throughout the polymer matrix (bulk erosion). The zero-order drug release can be rate limiting and primary factor only if the surface erosion occurs and the surface area almost remains constant [92, 93].

12.4.4 Osmosis

The rate at which drug exits from a delivery system can also be monitored by applying the process of osmosis in the design of a drug delivery system. One of the most important components in the design of an osmotic drug delivery system is the semi-permeable membrane [66].

The phenomena of osmosis exhibits migration of solvent molecules from the region of lower concentration to the region of higher concentration across a semi-permeable membrane. In this type of controlled drug delivery system, the drug (either in a solution or a solid form) and an osmotic agent are enclosed by a semi-permeable membrane having orifice for drug passage out of the system and thereby determines the rate of the drug release [94, 95]. The Liquid (solvent) influx monitors the rate of delivery of the drug via the semi-permeable membrane from an elementary osmotic system, in turn, it carries the drug out of the system through an opening. The transfer rate of a drug (impermeable) through the membrane is mathematically expressed by the given equation [96].

$$\frac{dm}{dt} = \frac{A}{h} L_p (\sigma \Delta \pi - \Delta P) \cdot C$$

Equation 12.2. Modified equation for osmotic delivery of drugs through Rose-Nelson pump

Where, " dm/dt " is the rate of drug transport across a semi-permeable membrane, " A " is the surface area of the semi-permeable membrane, " h " is the thickness, " L_p " is the mechanical permeability of membrane, " σ " is the reflection coefficient, " $\Delta\pi$ " is the osmotic pressure gradient across the membrane, " Δp " is the hydrostatic pressure difference across the membrane, and " C " is the concentration of drug in the distributed fluid.

12.5 Ideal Characteristics of Coating Polymers

12.5.1 Solubility

The solubility of coating polymer in a gastrointestinal fluid is a key factor for determining the application of polymer as immediate-release, delayed-release, and prolonged-release film coats. Furthermore, it also determines whether the coating polymer solution or suspension is sprayed or delivered as a pseudo latex or latex dispersion [97, 98].

12.5.2 Viscosity

The viscosity of coating polymers in solution is a limiting factor with regard to the ease of application and appearance of the finished dosage form. Highly viscous suspension having a viscosity greater than 400–500 mPas is difficult to spray. Lower viscosity suspensions having viscosity around 100 mPas or less are evenly sprayed and provide a smoother coat. To prevent settling of dispersed particles during coating, suspension must be continuously stirred [98, 99].

12.5.3 Permeability

Appropriate permeability is necessary for various functional properties of the polymer films. For barrier applications, moisture protection, and taste masking, low permeability is required while intrinsic permeability of the polymer films may be changed for some prolonged-release dosage forms by incorporating additional formulation components [98, 99].

12.5.4 Glass Transition Temperature

Glass Transition Temperature (T_g) expresses the molecular motion of the polymer which is dependent on many factors affecting polymer chain movement. Free volume, the empty space in between the ends of the

polymer chain, facilitates the segmental motion in polymers. Generally, polymers with higher Tg values are desirable as they enhance processing and handling qualities, dissolution and bioavailability, and physical stability. Long polymer chains having high molecular weight and polymers with polar and bulky side groups possess higher Tg values due to smaller free volumes. In comparison to branched and flexible polymers, linear and rigid polymer chains have higher Tg values. Similarly cross-linked chains have a higher Tg value due to higher entropy [98, 99].

12.5.5 Mechanical Strength

Polymer films with a high tensile strength provide better protection and are more resistant to cracking and splitting. Young's modulus and tensile strength are in a linear relationship with the molecular weight of the polymer. Higher the molecular weight greater the tensile strength and Young's modulus [98, 99].

12.6 Conclusion

The successful design of coated pharmaceutical product requires knowledge of the polymers, technologies and release mechanisms to ensure that the most appropriate system is adopted for the targeted drug. This chapter presents a broad overview of types of polymers, covering its characteristics, applications and commercialized systems using both natural and synthetic polymers. The variability of the polymer, with respect to diversified physico-chemical properties and stability also needs to be considered when deciding on a strategy for coated pharmaceutical product design. It is essential that the coating processes and coating formulations are carefully controlled and optimized to ensure batch to batch reproducibility of the product. Based on the valuable economic and clinical benefits that the coating polymers can provide, it is expected that the significance of polymers for coating pharmaceuticals will continue to evolve in the near future especially in the field of nanotechnology and target specific drug delivery system.

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Self-Healing Polymer Coatings

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Abstract

The critical characteristics of self-healing polymeric coatings are covered in this chapter. An outline of progress in existing self-healing coating methods and realistic frameworks of polymeric coatings are provided after elaborating the introduction and benefits on self-heal concepts in polymer coatings. Self-regeneration of surfaces and anti-corrosive protective layer fractures were discussed. Eventually, a current industrial applications and possible potential activity for the future prospect will also be discussed. This review aims to explore the fast expanding area of self-healing polymeric coatings by analyzing the main mechanisms that were effective in automatic repair over the past decade. Furthermore, some issues relating to the transition from laboratories to valid industrial application of these self-healing technologies were addressed.

Keywords: Coatings, self-healing, polymers, anti-corrosion, fractures, reliability, degradation, thin films

13.1 Introduction

Over decades, coatings have been considered as a desired material of importance. A layer or scheme of strata is used over a particular substratum mainly for three primary reasons: shielding, functionalization, and of cultural importance. There are a variety of plastics that need to be protected

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with coatings during their corresponding service life. Metal substrates, rocks, concrete, wood, leather, fabrics, polymers, composites, plastics, textiles, etc., are the most common coated materials. There are numerous coating formulations that can be used depending on the material to be protected and the essential coating properties. Inorganic, polymer, and artificial formulations are included in this case. It is not very obviously described about the extreme origin of coating materials. Many formulations, for example, lacquers, varnishes, enamels, bee wax, mineral clays, animal oil, and many more natural products, are renowned for millennia. The most common instant characteristics of coatings are decoration, aesthetic feel, luminosity, repellent, safety from corrosion, heat barrier, anti-fouling, wear resistance, and better lubrication.

Over the past few years, coating engineering has experienced enormous developments that will certainly remain in the close future. Today, there are many formulations, and they can simply not count the provided features. However, there are still inconveniences and fresh difficulties arises everyday as traditional and innovative high-tech functions require more functionality and shorter lives of coated products. Coatings for the corrosion safety of concrete plastic products have a considerable financial effect, because the coated layer determines the importance of the product in operation and also in its efficiency. For certain phases of moment, a safety layer must be sustainable, by maintaining its physical strength and operational characteristics. However, coatings are prone to fading during certain practical applications and the primary characteristics are progressively degraded. The degradation speed relies on several parameters, such as the physico-chemical design of the covering and substrate, the fabric size, and the internal environmental aggression. As a result, regular servicing is required necessarily, usually recoating or removing the exposed harmed components and replacing them. Currently, coating products with minimum internal interference that can last forever are ahead of the latest technology. There has been a number of study attempts to develop intelligent fabric products, particularly those with clever functions and self-healing characteristics. Intelligent self-curing coatings are an extremely interesting category of material. These categories of products with disruptive accomplishments have been the subject of numerous attempts in the last centuries. Among them, intelligent nanocontainer products are one of the most successful techniques for the development of self-healing coatings.

13.2 Self-Healing: Introduction and Benefits

The capacity to automatically and autonomously cure (recover/repair) injury can be characterized as the capability of a self-healing product, which is without any external interference. To identify such an asset in products, numerous popular words such as self-reparation, autonomy healing, and auto-reparation are used. Most often, it is impossible to incorporate the self-healing characteristics into human products without an exterior cause. So, the two kinds of self-healing are as follows:

- autonomous (no interference)
- non-autonomous (natural intervention/external triggering necessary)

Self-healing can be described in coating techniques as the complete or temporary restoration of matrices harmed by aging or unforeseen violent occurrences [1]. This idea has been expanded, including the activation of oxidation in metal surfaces. Most of the suggested alternatives recognized as highly efficient therapeutic products are considered to be extremely important. In order to bring self-healing functionality into organic or hybrid coatings, two key approaches were developed: (i) intelligent matrix response, enabling mitigation of failures created in the matrix because of the existence of artificial species, and (ii) portable and synthetic organisms encapsulation, giving special functionality. Among other species, they include monomers, polymers, inhibitors of corrosion, antifouling molecules, antibacterial drugs, etc. Outdoor or interior activities can trigger self-healing functions. Quick coating is thus a category of products that can detect harm and react to particular causes which lead to the discharge of active organisms that mitigate harm. The renowned self-healing techniques have been anticipated for smart responsive polymer matrix or for restricted discharge of efficient species from micro- or nano-containers susceptible to explicit triggers.

The fundamental concepts of a self-healing process in a safety layer are illustrated in Figure 13.1. A fracture is instigated in Figure 13.1(a), which expands so that the triggering procedure can be activated automatically. As a result, the curing agent is liberated which heals the harm caused by the layer, as seen in Figure 13.1(b). In order to reaffirm the barrier properties of the protective coating, this process is highly effective and provides

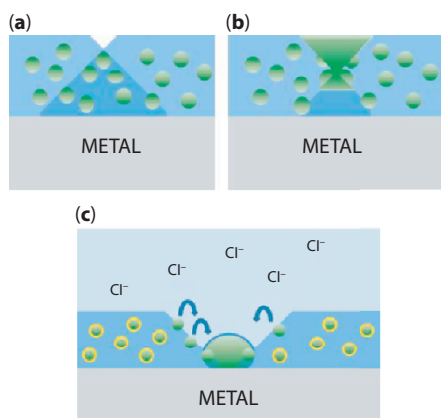


Figure 13.1 Schematic view of crack-induced self-healing processes. (a) A crack appears and develops affecting an internal area of the coating. The stress induced by the cracks breaks the reservoirs that release a mobile phase. (b) The mobile phase reacts and fills the crack, restoring the coating barrier properties. (c) The coating is damaged, exposing the bare metal, and a specific trigger (e.g., chloride ions activity) induces the release of the active healing agents stored inside the containers that repair the damaged areas. [With kind permission obtained from RightsLink, Elsevier License]

repair of the cover matrix. Figure 13.1(c) expresses the fully damaged coating layer and exposes the bare metal to natural environmental aggression. Containers packed with functional/repair organisms are caused by the existence of chloride ions because of continuing chemical and electrochemical interfacial modifications. The curative is discharged in the region affected by harmful occurrences, which inhibits the continuing decay procedures and cures the harmful region very effectively. Preferably, a demand/release-based series of occurrences should only operate when the harmful occurrences exists. The encapsulated object must be placed until the next occurrence after the harm has been cured.

Self-healing resources are not a myth anymore and the fact that man-made materials can recover structural reliability if they collapse. The fractures in walls can cover themselves or the marks on car bodies can restore their glossy unique exterior. Yes, this can be seen by everyone as wounds and cuts in living organisms are naturally healed. Almost all materials are susceptible and degradable in time to natural or artificial degradation. Roughly every product is prone and time-consuming to natural or artificial degradation. The long-term process of deterioration leads to micro-cracks that cause failure in case of construction materials. Repairing is therefore necessary to improve quality and material life. While researchers

are motivated by usual blood clotting procedure or the repair of fractured bones, it does not really take account of the difficult environment of cure procedure in human being or further animal systems [2–7]. Nevertheless, Nissan's latest declaration that scratch-healing paints should be released commercially on automobile cover has drawn communal attention in a marvelous estate of such products [8].

13.3 Summary of Progress in Self-Healing Coating Technology

13.3.1 Coatings for Self-Regeneration

The reduction in specific utility during a certain instance deteriorates adhesion between coat and substrate, UV-protection failure, unexpected weight alteration, anticorrosion function loss for metal substrate, and so on, can only be illustrated by the damage of a coating, as stated earlier. Therefore, the rebound of damaged connections may not be essential, since any layer does not benefit from failure or decrease of mechanical force. Rather, the harm to the coating layer must be cured by restoring the coating feature in a smart manner. The fact that a species may be a small molecule or else a loop linked en route for cross-linked arrangement gives some covering features. For example, small ground layer wettability arises from fluorinated or silicone-based strings; an effective corrosion inhibitor can be introduced for the benefit of anti-corrosion purposes.

To regain the role of coating, the particular species must be transferred or they may transfer to the location where the layer feature decreases in a “self-regenerating” way. In particular, surface energy, climate modifications, and others can be the guiding power of these particular species and should also be able to benefit from a certain degree of flexibility for comparatively fast transport within a coating system. One instance of the self-regenerating coating is a corrosion-resistant coating in which the scratch agent replenishes at the layer/metal interaction [9]. Some other researchers [10] have followed layer-by-layer installation procedure to pinch the wind controller on silica nanoparticles and have added nano-servois to the ZrO_2 and SiO_2 solar gel placed on an aluminum substrate in epoxy-functionalized coatings. During corrosion of the aluminum alloy, benzotriazole is released through pH modifications.

Another instance is the self-regeneration coating with low adherence. The coated layer is very crucial and regulates the weight resistance and

refraction. The ground structure of a layer is well recognized to be considerably different from its core structure. Low adhesion coatings have been used extensively today as their water/oil repellency allows them to be cleaned readily. Fluorine or silicone containing species at the film layer provide the low-surface stress. The ground segregation of fluorinated species has already produced low adherence coatings [11–15]. However, the fluorinated layer was shown to be very thin [14] and may not have poor adhesion to mechanical abrasion. Lately, independent regenerating strategy was created to maintain adherence properties as minimum as possible for fluorinated polyurethane coating [16]. However, the two main characteristics of this strategy are as follows: (1) fluorinated tails miscibility with the same polyester structure, and (2) the distance is supported by poly (p-caprolactone) (PCL), which allows sufficient flexibility of the fluorinated body when integrated into the interconnected networks. In the event of surface fracture leading to the failure of upper parts of the coating, fluorinated tails from sub-layers can be redirected to reduce the interface energy, because of the PCLs flexibility. Controlled functional procurators of polyester model have been produced through perfluoroalkyl liquor which regulates ring-opening polymerization of β -caprolactone [17]. In order to achieve films of minimum surface energy, suitable precursors be healed by means of cross-linking polyisocyanate. Fluorinated species with self-regeneration performance was proved in conjunction with microtoming through XPS analysis [16].

Figure 13.2 shows that the F/C molar proportion throughout the film seems consistent, which means that the allocation of fluorinated species

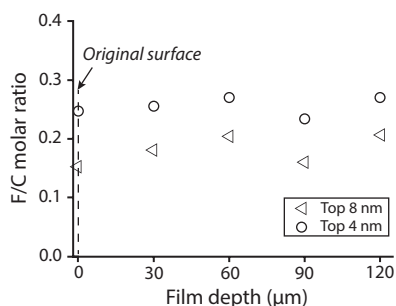


Figure 13.2 F/C ratios at two different probe depths (4 and 8 nm) for thin slices cut from a polyurethane coating containing perfluorooctyl-PCL (Rf8-PCL). The coating examined was prepared from a reaction mixture (Rf8-PCL, a PCL based polyol, and a polyisocyanate cross-linker). The coating was about 200 μm thick and contained 1wt% of fluorine. Thin slices of about 30 μm thick were cut by microtoming and the top surfaces of the slices were then examined by XPS.

in most of the film is comparatively homogenous. Another important thing is that 4 nm on upper side has 60% higher ratio on F/C for each slice compared to 8 mm. This obviously indicates that fluorinated tails are replenished following by microtoming prior to XPS experiment. Since the coating temperature of a glass transition region is approximately -20°C , self-regeneration of materials requires microtoming on chamber heat. Fluorinated tissue regeneration relies on the flexibility and heat of the polymeric networks. If the polymeric network has a temperature at glass transition region near the room temperature, fluorinated species may be regenerated simultaneously with the formation of a new surface. The regenerating behavior can be considered to be independent in this regard. This auto-recovery approach can be expanded to other active coatings like antimicrobial, biocidal, etc.

13.3.2 Anti-Corrosion Protective Layer Fractures

Arrangements and representations of the newly developed shape memory by Xiao fan Luo *et al.* [18] helped to self-heal the SMASH coatings (Figure 13.3). The coatings integrated a phase-installed morphology with the subjective transmission of electro-spun thermoplastic fiber (PCL) threads into a storage epoxy lattice. Mechanical damage to coatings may usually be caused by warming, resulting in two occurrences: first the matrix's restoration of form in space, and secondly, the dissolution and streams of PCL fibers to rebound from the break. In supervised trials, the damaged coatings basically and for all reasons repair it carefully. This correspondence shows the diagram and course of action for self-recovery

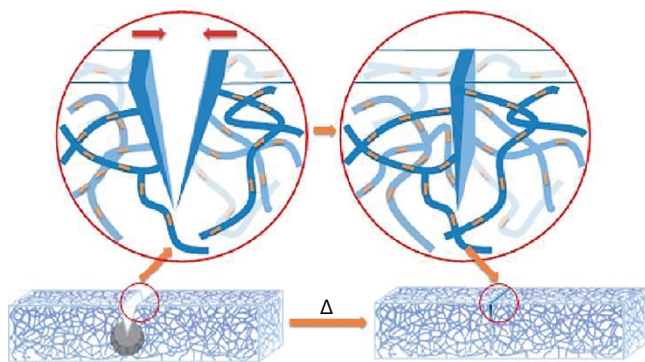


Figure 13.3 Schematic illustration of the coating morphology and the shape memory assisted self-healing (SMASH) concept.

systems with a self-regenerating component. The self-recovery was demonstrated by a fully reinstated block protection. In addition to this material development and composition analysis, there are different possible applications.

Mikhail L. Zheludkevich *et al.* [19] propose a different methodology of disintegration on request, which provides insightful self-recovery of the mutt sol-gel protected films. Controllable transportation in quarter and quarter of pretreatments is simplified, mixing the nano-levels of the benzotriazole inhibitor. The nano-compartments are restricted by silica nanoparticles securely LbL with nano-inhibitor polyelectrolyte ions. However, silica zirconia hybrid film containing 2024 aluminum compound provides an anti-corrosion effect. Silica nanoparticles protected layer-by-layer with polyelectrolyte strands and inhibitor materials which were placed in half-breed films. The impregnation of half-rate sol-gel films produces shield for the entire execution of metallic materials disintegration.

Dmitry O. Grigoriev *et al.* [20] controlled the discharges of polyelectrolyte compounds which can be used to manufacture vibrant coatings with fast cover. In specific, the capability to discharge anticorrosive actions of main coating is demonstrated by self-regenerating layers with complicated coating materials (Figure 13.4). The advantages of polyethylenimine (PEI) in antagonistic loaded SiO_2 nanoparticles were obtained by incorporating 20 ml of 15 wt.% SiO_2 solution. Nanocomposite multi-layer levels, colloiddally templated lithers and nanosticks with solidified inhibitors are used to prevent new protected products from damage. As an assistant, inorganic aid or in-porous inorganic particle is interlinked with the disintegration inhibitor.

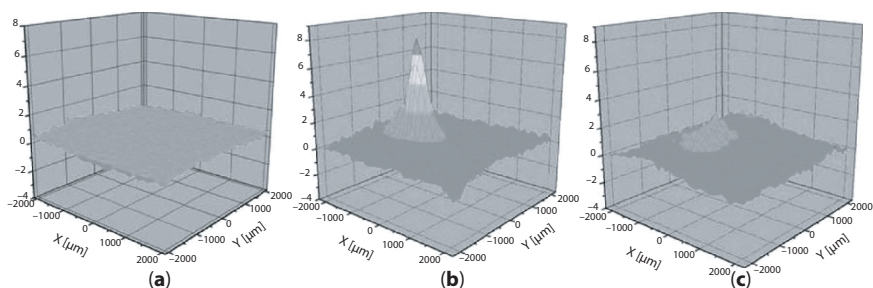


Figure 13.4 Self-healing of anticorrosion coating on AA2024 doped by micro containers with PSS/BTA complexes. Scanning vibrating electrode (SVET) measurements data collected: (a) immediately after immersion of AA2024 specimen into 0.1 M NaCl solution; (b) 42 h after immersion; (c) 60 h after immersion. Z-coordinates in all plots represent the local current density reflecting the development of the corrosion process.

13.4 Realistic Frameworks of Self-Healing Polymeric Coatings

Numerous self-healing method outlined within this analysis be confined to thin films, large polymers, coatings, and composites. So, thin layers can be applied to polymers that cure by UV-initiated bond. Healing incentive of UV irradiation has been entailed in these polymers. In addition, artificial UV resources cannot have penetrating lengths reaching the center of bulk polymers. Also, additional polymers with self-healing nature have also been recognized to comprise comparatively poor heating performances or fragile technical characteristics, which may be restricted to film and coating applications [21].

In contrast, a number of self-cure processes can able to employ only on polymeric composites. Most of this is due to the mass and quantity demands of certain therapeutic agents which have a higher thickness than typical thin film thicknesses [22, 23]. For comparable purposes, the healing product packed with hollow fibers is also confined to mass polymers. However, the self-healing polymers based on the microcapsules are not restricted as like the systems of microvascular and hollow fibres. The self-healing polymer microcapsules are most efficient at a scale of 100–200 μm , generally considered to be excessively huge on behalf of thin films [24]. However, current stories regarding nano-sized microcapsule-incorporated healing agents [25] possibly will lead to thin coatings in the area of microcapsule-related self-curing purposes. Even though it is likely adapted for mass implementations, the production in thin films of self-healing structures comprising phase-separated thermoplastic polymers may not be as impeded as several of the above-mentioned processes. Even if not yet published on in the literature, conventional methods of handling freeze could probably reduce EMAA and epoxy substances [26–28]. The PCL reactor stimulated phase-separation epoxy-polymers be particularly adaptable into applications of thin film, since the inherent PCL phase distribution divides on a micron level [29], eradicating the necessitate on behalf of further handing out measures on the road to diminish the amount of therapeutic agent.

13.5 Potential Historic Activity

Design and growth of intelligent self-healing nanocontainer polymer lacquers for multi-substrate functionality and safety is a difficult area of

studies that offers many possibilities. One of these is certainly protective against corrosion of metals. Current industrial sector needs more efficient coatings to ensure that metal components are protected for longer periods of time. The goal is to decrease the cost of servicing and production activity. Other characteristics like superhydrophobicity and antimicrobial are necessary in relation to corrosive prevention. The capacity to automatically cure plastic damages, corrosion startups, improved mechanical characteristics, superhydrophobic, or anti-icing characteristics mixing long-term obstacle characteristics are beyond the focus, for instance, to safeguard costly asset in offshore wind power generation.

On another side, the tendency is to reduce the weight of parts in many applications by merging lightweight resources with increased effectiveness. The solution to this requirement is to use multi-metallic or non-metallic components combined with metallic materials. These mixes involve entirely a bright ways of protection against corrosion. The use in metallic or non-metallic products was commonly researched, but the latest research to advance the approach in multi-material mixes is not found to be feasible. Nowadays, standard and recent hi-tech applications often utilize multi-material assemblies, which require entirely clean layer architectures accommodating substrates with very distinct characteristics. Numerous fields like biomedicine, sport, car industry, and aircraft division; this is certainly an area of extreme importance. Thinner coatings are screened to reduce number of layers and its density. To maintain the necessary efficiency, coatings must contain distinct functions which enable individual surfaces to show a variety of features and to meet several needs. Thinner coatings with improved protection against corrosion and a strong esthetic quality are very much required in the automotive industry. Additional features like superhydrophobicity, anti-dust and anti-fingerprint treatment, and heal and soft touch also apply to mobile devices, home appliance, and furniture. Smart self-healing coatings for unusual appliances like biomedical, power stove, cabling, electronics, and digital panel panels are also in a part of recent new developments. There is no doubt that the area of smart multi-substrates protective coatings will develop quickly in the coming years, with encapsulation technology taking a main part in resolving many critical problems.

13.6 Conclusions

The various limitations of different materials in engineering disciplines include high maintenance and repair costs. It is very difficult to repair at

remote locations. Therefore, self-healing coatings have enormous potential to improve the durability of structural materials. Hence, a large number of educational and industrial research organizations were included in this ambitious profile to explore new concepts. All government and industrial financing agencies are also showing a growing trend in investment. This paper explores a comprehensive literature assessment on research and development in self-healing polymeric coating materials. Specific solutions to self-healing substances like creeping cavity and resistance to fatigue cracks are explained in detail. In order to understand their uses, the self-healing mechanism is also studied. Damaged problems related to materials and corrosion protections are also examined for surface cracks. The unique properties of self-healing materials provide the system a new choice in different applications. These coatings can be used in many applications including spaceships, nuclear reactors, turbine injectors, and special cutting tools. Thus, automatic crack detection and eventual healing are the main challenge for design of self-healing polymeric coating materials. This wonderful area of self-healing polymer coatings will undoubtedly continue to grow beyond the technologies discussed in the above sections and will be accessible for daily use.

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Polymer Coatings for Biomedical Applications

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Abstract

Over the years, polymer coating has evolved as a fascinating tool for surface functionalization of materials usable in a wide range of fields. The polymer coated surfaces have been used for infectious therapy, drug delivery system for therapeutic agent, and protective layer for implants and biomedical devices. The chapter highlights some key developments in the field of polymer coating which were trend-setting for its applications especially in biomedical science.

Keywords: Polymer coating, biomedical applications

14.1 Introduction

Over the last few decades, the increasing consciousness about disease-treatment related risks have surged the development of new risk-free treatment strategies and medical devices. The traditional style medical devices pose serious threats of infection when come in contact with human body. As a result of increasing concerns, the synthesis of novel materials for biomedical applications has become an attractive area of research. In this context,

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a lot of efforts have also been made to modify the surfaces of medical devices to induce health-safety features like biocompatibility, non-adhesion of microbes, and prevention of non-specific binding of proteins which otherwise cause fouling. Over the last few years, the aforesaid health-safety features are induced in biomedical devices and implants through polymer coatings on in-contact surfaces [1].

The polymer coating provides tailored surface chemistry which enhances corrosion protection and improves mechanical strength, electrical conductivity, and water resistance characteristics to materials. Over the last decade, the tremendous developments in the synthesis of stimuli-responsive, smart-, shape memory, and conductive polymers of natural and synthetic origin (Figures 14.1 and 14.2) have revolutionized the fabrication of implants and medical devices. Owing to these excellent developments, the polymer coatings have widely been used to acquire characteristic features in biomedical applications [2, 3].

In current scenario, the adhesion, proliferation, and differentiation of cells have become controllable phenomena due to the surface-mediated tunable properties of polymer coatings. The polymer coating-mediated

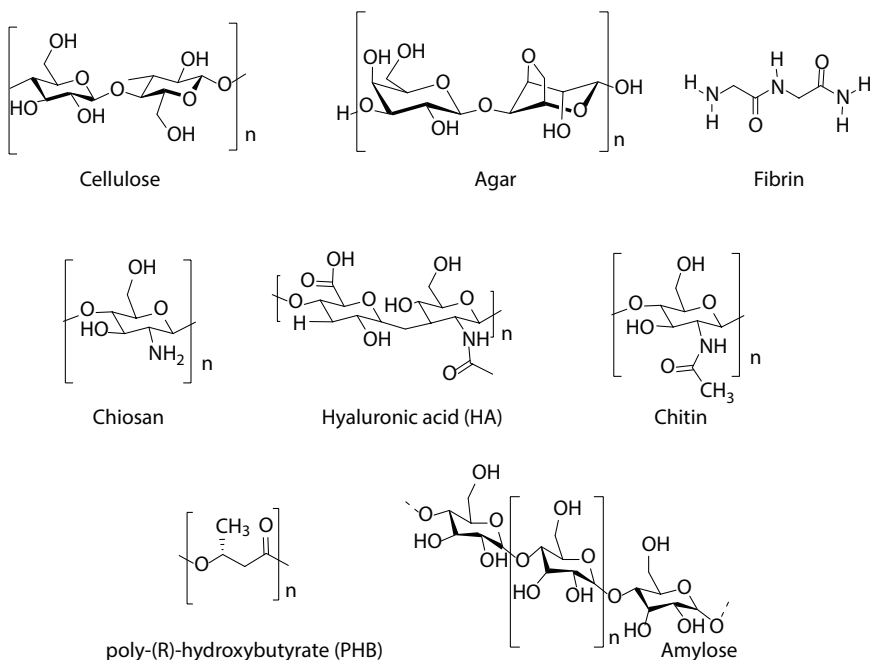


Figure 14.1 Natural polymers frequently used for coating.

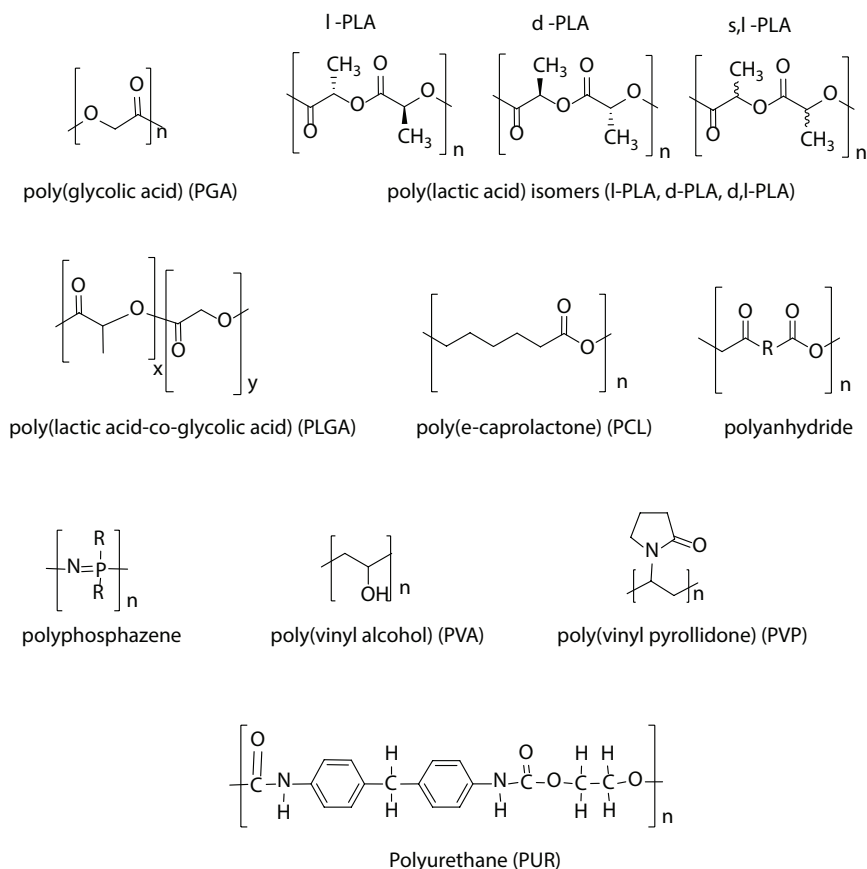


Figure 14.2 Natural polymers frequently used for coating.

guided cell/surface interactions have also opened up new horizons for guided tissue engineering. Using polymer coatings, the surface-mediated controlling of non-specific interactions are also used to produce anti-fouling properties on medical devices which often come in contacts with biological fluids. The approach has also gained considerable attention in context of sustained and controlled release of drugs. The polymeric coatings have also demonstrated their worth as potent drug delivery systems especially for those drugs which show promising therapeutic potential but low water solubility and bioavailability [4]. The recent developments in polymer coating have made it a new strategic tool with wide applications across many scientific domains. It has become a promising tool with ever increasing applications in orthopedics, bio-sensing, diagnostics, and targeted delivery of therapeutic agents.

The subsequent sections highlight some key developments and applications of polymer coating in biomedical field under the headings of tissue engineering, drug delivery, and antimicrobial surfaces.

14.2 Applications in Tissue Engineering

The elasticity and biocompatibility are the characteristic features of polymers which make them suitable candidates for applications in tissue engineering as coating materials. Over the few decades, the naturally occurring polymers including chitin, cellulose, alginate, gelatin, and cellulose has widely been employed as coating materials in tissue engineering due to above-said much needed features. Similarly, a number of synthetic polymers have proved their potential as superlative coating materials in tissue engineering.

The field of regenerative medicines has really been under high expectations to provide treatment strategies for diseased and damaged tissues through an easy generation of functional tissues and organs. There has always been a challenge to setup an ideal integration between material science approaches and principles of cell biology for three-dimensional growth of cells and tissues. Over the last few years, the *in vitro* generation of tissues has become a reality due to the recent advancements in both disciplines [5]. The engineered tissues show fully differentiated cells expressing protein profiles identical to the original ones. However, modulation of cell growth, tissue generation and morphology pose real-time challenges and require specialized hands to employ complex design and approaches. Very recently, chitosan-based coating has been used to modulate cell and tissue growth in *ex vivo* culture substrate. This facile, simple, and reproducible technique helped to control cell behavior, growth, and functions just by concentration of chitosan coating [6].

During the growth and tissue development stages, the cellular microenvironment experiences drastic changes in mechanical properties. The cells do sense the physical changes and mechanical stresses and show a responsive modulation in growth, organization, and tissue morphogenesis [7]. However, such mechanosensitive reactions of cells and their consequences on tissue morphology remain largely unknown. The understanding of such mechanosensitive responses of growing cells may help to control the regeneration of damaged tissues. Such mechanistic insights may also be adapted to regulate the size and morphology of artificially growing tissues. In one such study, the alginate-based polymeric hydrogel coating was used

to create a biomimetic microenvironment with aim to evaluate the effects of physical cues on tissue morphology during *in vitro* tissue synthesis. Miyajima *et al.* found hydrogel-based microenvironment as guide, modulating the size and morphology of developmental submandibular gland (SMG). The softer gel enhanced the cleft formation and bud expansion of SMG while stiffer gel formulation attenuated them. This study presented an excellent example of polymeric coating applied as biomimetic cellular microenvironment for controlled tissue morphogenesis [8].

Sato *et al.* employed poly (L-lactic acid-co-ε-caprolactone) coating as protective layer on luminal surface during artificial reconstruction of tracheobronchial in canine model. In fact, polymer coating protected the collagen layer and promoted the luminal epithelization. In the absence of such biodegradable protective coatings, the collagen layer undergoes early disintegration causing epithelization process incomplete [9].

In guided tissues regeneration technique, the barrier membranes are used as physical barriers for the deflection of growing tissues in defected regions. These physical barriers reduce the growth of competing connective tissue and only allow the fast regeneration of periodontal ligament fibroblasts. Such membranes are expected to control the migration of epithelial cells, stabilize wound site and prevent infections. Further, they are require to show space maintaining ability, cell viability, biocompatibility, and bioactivity during guided tissue regeneration period [10, 11]. In this connection, collagen-based resorbable membranes and expanded polytetrafluoroethylene (ePTFE)-based membranes are commercially available. However, the applications of these available membranes have met limited success as collagen-based membranes cause localize inflammation and show fast degradation while ePTFE-based membranes need surgical operation for their removal [12].

Chen *et al.* used chitosan to prepare GTR-membrane with one side coated with alginate to induce biocompatibility with minimum toxicity. They performed cell adhesion test, degradation behavior, and mechanical strength of the uncoated and coated sides of the membrane to evaluate the feasible application of such membrane in GTR-technique. In cell adhesion test, 3T3 fibroblasts exhibited about 50% low adhesion on alginate-coated surface compared to non-coated side of the chitosan membrane. The alginate coated side displayed different surface morphology and hydrophilicity as it showed decreased contact angle and higher water contents. The alginate coated chitosan membrane was suggested as an ideal candidate for GTR for controlling the growth of competing hard tissue (alveolar bone) while promoting the growth of soft tissue (gingival tissue) [13].

In conditions of blood vessel fistulas and aneurysms, the vascular grafting with high safety profile has become the leading treatment option over the last few decades. Mainly healthy blood veins are removed and implanted to replace diseased arteries in patients as an autografting strategy. However, in cases where patient had already undergone autografting or pre-existing diseased vessels, the polymer-based materials are employed for the replacement of diseased vessels [14].

Such vascular grafts of medium to large diameter are generally prepared from polyethylene terephthalate (PET). The biological performance and long-term potency of vascular grafts depends on the porosity of the polymeric material. The high porosity of grafts causes blood leakage during implantation and considered as a big disadvantage of vascular grafting. Before implantation, the permeability of grafts is reduced by using certain sealant or preclotting with patient's own blood. Over the past few years, polymeric materials have become attractive choices to control the porosity of vessel grafts due to their biocompatible and biodegradable nature [15].

Manju *et al.* used oxidized alginate and gelatin to develop a polymeric hydrogel which was coated on the PET graft to control the porosity. The efficacy coated grafts was evaluated by investigating adhesion and proliferation of endothelial cells (EC), hemocompatibility, *in vitro* cell culture toxicity, burst strength, and water permeability. The results suggested that coating of PET reduced its hemolytic potential, posed no change in burst strength, and enhanced the adhesions and proliferations of EC. The biocompatible and biodegradable coating sealed the pores efficiently but did not affect the mechanical properties of graft [16].

In recent years, the bone tissue engineering has demanded the development of polymer-ceramic composites due to the highly complex composite nature of bone tissue. An ideal scaffold is expected to have well-harmonized structure of inorganic and organic components with ability to deliver cells, excellent osteoconductivity, and biodegradability. The ability to promote bone formation has made bioactive glass ceramics and silicate glasses as attractive entities in TE.

Considering the above facts, Erol *et al.* used boron-containing bioactive glass to develop novel scaffolds which were further coated with alginate cross-linked with Cu ions. This novel scaffold with controlled Cu-releasing ability was designed to enhance angiogenesis. The alginate coated scaffold higher compression strength, improved bioactive behavior, and elevated angiogenic potential compared to non-coated scaffold in *in vitro* bone regeneration studies.

14.3 Polymer Coating for Drug Delivery

In recent times, the excellent surface mechanical properties and controllable porosity have highlighted the role of polymeric scaffold in TE. As discussed earlier, such scaffolds are prepared from highly biocompatible biomaterials so they do not provoke any reaction against foreign invaders and there have always been excessive chances of infections. Clinically, injections are practiced regularly to reduce infection before it worsens the situation. Most of the times, patients face potential side effects due to higher drug concentration in blood. The biocompatible scaffold with extra advantageous of a local drug delivery system is required to control such unavoidable on-site infections without disturbing the bone regeneration process. Such local drug delivery systems are expected to show predictable therapeutic response, greater efficacy, and sustained drug release with ideal safety profiles [17, 18].

Huang *et al.* developed a novel scaffold carrying drug-loaded chitosan coating to confront infections during bone tissue regeneration. The nano-hydroxyapatite/polyamide66 (n-HA/PA66) scaffold was coated with chitosan loaded with berberine (antibacterial drug). Different ratios of CS and berberine were used to study drug releasing behavior, mechanical properties, and morphology. They suggested that the compression strength and elastic modulus of coated scaffold was much higher than the uncoated scaffold. Depending on the coating concentration, the burst drug release appeared in first 3 hrs and a continuous release was detected for 150 hrs in phosphate-buffered saline solution. The controlling of drug release by the coating concentration is highly suited requirement for infection therapy in bone tissue engineering. The MG63 cells exhibited enhanced adhesion, growth, and proliferation on coated scaffold which suggested the non-toxic nature of drug-loaded coating. The results suggested the potential applications of coated scaffolds in bone defect repair and TE [19].

Over the last few decades, curcumin, a natural lipophilic polyphenol, has established its worth in chemotherapy against a variety of cancers including breast, bone, gastrointestinal, lung, and prostate cancers. It is also known as multitherapeutic agent due to a range of bioactivities including anti-oxidant, anti-HIV, anti-amyloid, anti-inflammatory, and anti-malarial, etc. However, the clinical applications of this phenomenal drug has always been restricted due to poor water solubility, fast metabolic degradation, thus low bioavailability [20]. In last few years, the recent advances in nanotechnology have accelerated the development of nano-carrier systems for poorly water soluble drugs to enhance their stability and bioavailability [21, 22].

Quite recently, solid lipid nanoparticles (SLNs) have become attractive nanodrug delivery systems because of their ability to encapsulate lipophilic drugs in larger quantities. Ramalingam *et al.* enhanced the bioavailability and stability of curcumin by developing SNLs-coated with chitosan. The chitosan coated mucoadhesive SNLs enhanced the oral bioavailability and physical stability of curcumin [23].

In another study, the chitosan coating found to produce a thick layer on SLNs under gastric conditions thus enhanced their stability. In fact, mechanistic electrostatic repulsions and steric stabilization of chitosan coating ensure the stability of SLNs. It was concluded that chitosan coating improved mucoadhesion, cellular uptake, stability, and controlled delivery of hydrophobic drug [24].

The low molecular weight heparin (LMWH) is well-known for its anti-angiogenic activity and employed to inhibit progression of cancer and as therapeutic agent for rheumatoid arthritis. It also shows anticoagulation activity in the treatment of pulmonary embolism, deep vein thrombosis, and venous thromboembolism. Advantageously, it does not induce any toxic effects like bleeding and thrombocytopenia like heparin. However, poor penetration through intestinal wall, high negative charge, and high water solubility has restricted its applications through parental route only. Over the last few years, chemical conjugates and penetration enhancer have been employed to develop effective oral therapy for improved patient compliance [25].

Bagre *et al.* used LMW enoxaparin to develop oral delivery system as alginate-coated chitosan core shell nanoparticles (Alg-CS-NPs). Alginate is known for its non-risky ability for controlled and sustained oral drug delivery. The *in vitro* particulate uptake and permeation across intestinal epithelium, drug release profile, and pharmacokinetic studies were performed to evaluate the efficacy of Alg-CS-NPs. This new oral delivery system enhanced the oral bioavailability and gastrointestinal uptake of LMW enoxaparin thus reduced the above-said limitations in oral therapy [26].

The conventional cancer therapeutic options like chemotherapy always produce severe side-effects with low efficacy. In current era of nanotechnology developments, a number of drug delivery systems have been introduced for controlled drug delivery. The existing delivery systems for cancer therapeutics utilize liposomes, silica-based porous materials, dendimer-based micelles, and polymeric systems. These drug delivery systems still show limitations as they require complex preparatory procedures and highly skilled human resource so they are expensive for a large population of world [27, 28].

Over the last few years, the attentions have been diverted to explore novel vectors for sustained delivery of anticancer agents with minimum limitations. In this connection, Zhu *et al.* used bacterial vector as delivery agents for sustained release of polypeptide exotoxin A which blocks protein synthesis in eukaryotic cells thus cause cell death. The delivery system employed bacterium as nano-carrier, toxin PE66as anticancer agents, and combined coating of CP and polymyxin B (PLB) for ROS triggered sustained and controlled release. This system proved as a brand new dimension in encapsulated anticancer therapy for delivery and release of drugs [29].

The DNA-based vaccine therapy has emerged as an attractive field due to the capability to promote humoral and cellular immune responses, and lack of anti-vector immunity. However, the initial trials in human and non-human primates exhibited poor plasmid DNA immunization. A number of disadvantages are exhibited by both traditional needle-based administration of vaccines and advanced DNA vaccination technologies. The vaccination distribution has really become a problematic issue especially in developing world.

An approach can substantially enhance DNA vaccine delivery which can simultaneously induce potent immune response, promote non-toxic and sustained transfection, and target DNA in immune-cell-rich tissues. DeMuth *et al.* developed a polymer film loaded with vaccine carrying biodegradable polycations, immune stimulatory RNA and DNA. The vaccine-loaded film was implanted into the immune-cell-rich epidermis using releasable polyelectrolyte coated microneedles. In non-human primates, this DNA vaccination enhanced gene expression 140 folds compared to intradermal injections also increased memory T-cell generation. This new DNA vaccine also induced immune response against a model HIV-antigen. So, the new DNA vaccination strategy exhibited its potential against traditional as well as newly available techniques.

14.4 Polymer Coating as Antimicrobial Surfaces

In recent times, the poly(dimethylsiloxane) (PDMS) has emerged as an ideal choice to prepare contact lenses, catheters, pacemaker encapsulants, and surgical implants. Recently, its characteristic features like elastomeric properties, low toxicity, and biocompatibility have driven its applications in biosensors, DNA sequencing, diagnostics, and drug delivery. However, microbial adhesions and protein/hydrophobic analyte adsorptions cause biofouling problems due to low wettability of PDMS. Such safety issues

restrict the PDMS-based devices especially which come in contact with microfluids like blood. In order to encounter such performance-limiting conditions, a number of physical approaches and chemical treatments have been adopted to induce hydrophilicity and anti-fouling characteristics on PDMS surface. Its surface state is changed via electrostatic or hydrophobic interactions by adsorption of coating material in physical methods. In some other physical treatments, its surface is activated by UV light, ozone or oxygen plasma treatment. However, all these physical treatments serve temporarily and the hydrophobic surface is recovered with passage of time. While chemical modifications changed the surface permanently and induce long-lasting anti-fouling characteristics [30].

As a part of chemical treatments, a number of polymer coatings could be applied to enhance wettability of PDMS surface. In this regard, the coating with hydroxyl-enriched polymers has been preferred for high hydrophilicity due to the abundant of hydrogen bond formation [31]. The anti-fouling performance is strongly correlated to the hydration layer formed on the surface. The PDMS microfluid chips were coated with polyvinyl alcohol (PVA). The PVA coating induced anti-fouling properties by preventing the adsorption of proteins both in acidic and basic media. The results suggested the applications of PVA coated PDMS-based implants while dealing with microfluids like blood, etc [32].

The microbial wound contamination is a main side problem with orthopedic operations under trauma and disease conditions. Such contaminations lead to infections which delay the recovery process putting impact on patient's health. In case of bone fractures, the internal fixation with infections can be dangerous while it helps to regenerate bone with stable fractures. Under such conditions, the implanted biomaterials could serve to provide infection therapy [33, 34].

Generally, bone fracture is fixed using internal fixation devices made up of stainless steel. Greene *et al.* coated the bone screw fixation with chitosan loaded with gentamicin, a known antibacterial agent. The chitosan coated bone screws were found biocompatible with stem cells and fibroblasts. The sustain release of drug was detected for 72 to 96 hrs and exhibited its antibacterial activity against *Staphylococcus aureus*. The results suggested the suitability of chitosan as potent bonding material for stainless steel orthopedic devices with extra advantage to carry therapeutic agents [35].

The biocompatibility, corrosion resistance, strength to weight ratio, and mechanical properties have increased the use of titanium and its alloys for the fabrication of biological implants. Especially, it is used to manufacture dental and orthopedic implants for longer service life. However, the so-called stable oxide layer on its surface gets rough with passage of time

thus limits the life of implants in biological fluids. Such conditions ultimately cause infections and result in diseased conditions [36].

Swanson *et al.* developed chitosan loaded with vancomycin coating for titanium implants. They studied the drug releasing behavior of polymer coating with respect to the standard drug. The results suggested the tailoring of coating surface with anti-infectious features. They introduced concept of titanium-based safer biological implants with efficiency to prevent infections through local drug delivery by protective polymeric coating [37].

14.5 Conclusion

Functional polymer coatings have found wide spread application across many specific disciplines. It has emerged as a powerful tool capable of functionalizing the material surfaces with desired characteristics. The recent advances in polymer science have revolutionized the role of this fascinating strategy in biological science especially in biomedical applications. The chapter highlighted some key applications which were trend-setting for surface functionalization of implants and biomedical material. The recent development in polymer functionalization and coating technique reflects a promising feature of this fascinating tool.

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Antimicrobial Polymer Coating

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Abstract

Antimicrobial polymers are the type of polymers having the ability to inhibit or kill the growth of microorganisms such as bacteria, protozoans, and fungi. These polymers mimic the action of antimicrobial peptides which are utilized by the immune systems of such living organisms to kill the bacteria. The main purpose is to develop a self-decontaminating coating that has bactericidal effect to kill the microorganisms when they are come to contact with the antimicrobial surface. Antimicrobial polymer coating is widely used in controlled drug delivery system and implants in dental restorative materials. Antibacterial surfaces may exhibit antibiofouling effector inactivate the cells when they come into contact with surface for repulsion or the resistance of initial attachment of bacteria. Because they have biocidal activity, metals are used in antimicrobial polymer as antimicrobial agents. Metals, copper, and silver, are highly toxic to bacteria even at low concentration. These antimicrobial agents release over time and prolong the lifetime of antimicrobial properties of system. The use of antimicrobial polymer is to treat the microbial infections which become more difficult due to resistant of microbial strains, to enhance the activity of some pre-existing antimicrobial agents and to prolong the effect of antimicrobial agents. The major purpose of antimicrobial coating is to combat antimicrobial resistance and infections.

Keywords: Mechanism of action, hydrophilicity medical device applications, charge density, medical applications

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15.1 Introduction

Microbes such as fungi, bacteria, and parasites are the source of infections. Pathogenic microbes are responsible for infectious diseases. Antimicrobial agents are utilized to kill the micro-organisms or inhibit microbial growth. Many antimicrobial drugs have been introduced to treat with infectious diseases [1]. Infection is critically associated with implanted medical devices. These infections include premature device failure, tissue destruction, and spread of infections to other areas. The adherence of microbes with biomaterial is a major key factor for the initiation of an infectious disease [2]. There are many ways through which infectious diseases can spread; approximately 50% of all types of microbial infections are due to the contaminated surfaces [3]. The biofilm formation on the surface is major issue related to infection. There is a need to develop the coating that prevent the formation of biofilm or eliminated the already constructed biofilm. Antimicrobial coating can kill the microbes before and after contact with surface and prevent adhesion of bacteria. Recent research studies also develop new antimicrobial polymer coating having the dual action biocidal action. Biocidal material and surfaces have better biocidal activity and effect for longer period. Antimicrobial polymer coating perform dual action as biocidal materials and surfaces by a simultaneously contact killing and biocidal released action. Quaternary Ammonium group covalently incorporated into polymeric substrate or polymeric chain is responsible for contact killing actions. Many polymeric materials have the ability to leach out biocidal agents. The example of such polymeric materials includes inorganic metal nanoparticles or some antibiotics that are responsible for released based biocidal action [4].

Metals are widely used as antimicrobial agents due to its biocidal activity in agriculture, industry, and in health care system. Non-essential metal such as silver is toxic to bacteria having biocidal activity at very low concentrations. Essential metal such as copper is lethal to bacteria. Nowadays, metal oxides and their salts based on copper and silver are used as antimicrobial agents. Silver is highly expensive metal so their salts can be used. Copper is a cheaper than silver but it prevents the corrosion. To overcome this problem, metal oxide can be used as antimicrobial agents [5].

Antimicrobial polymers are such substances that have ability to kill the microbes and inhibit the growth of microorganisms on any surface or any surrounding environment. Some antimicrobial agents have an inherited ability to exhibit the antimicrobial activity. The examples of such antimicrobial agents are chitosan, many compounds having the quaternary

nitrogen groups, halamines, and poly- ϵ -lysine (ϵ -PL). Some antimicrobial polymers act as a backbone for incorporation of small biocides and these antibiotics also display their antimicrobial activity [4]. An ideal antimicrobial polymers should have the following characteristics a) broad spectrum for pathogenic microorganisms, b) exhibit the long term activity, c) should be stable and have no toxicity, d) can be easily synthesized and inexpensive, and e) can be regenerated when it lost its activity [6].

The antimicrobial polymers coating is an effective method for wide range of applications such as covalent and non-covalent bonding. Recent research has developed antimicrobial peptides-based antimicrobial hydrogels, antimicrobial polymer, and surfaces. In our daily life, we have to face many surfaces which are may be responsible for infections. Because such type of surfaces may act as highly potent reservoirs of many deadly pathogens and these pathogens form the biofilms which are core reasons for most of infections. For the limitation of surface associated infections, some strategy should be adopted such as preventing the adherence of microbes with biomedical devices and inhibit the colonization of microbes on the biomedical devices and other associated surfaces. This is possible if coating of surfaces is done by antimicrobial polymers. To inhibit the presence and colonization of the microbes on many surfaces, polymeric coating is a very effective strategy. Depending upon the applications, various types of polymeric substances can be used. The major purpose is to combat antimicrobial resistance and infections [3].

Polymers are used in the recent years as a substituent of many metal, wood, and glass in many applications because polymers have many physicochemical properties as well as economical. Table 15.1 shows the polymer medical device application [7].

15.2 Mechanism of Action

The technique for designing of antimicrobial polymers is to determine the structural characters of the outer most envelope of the bacterial cell. The outer envelope of the cells has negative charge. Gram-positive bacteria cell wall (CW) has teichoic acid, the outer membrane (OM) of Gram-negative bacteria has phospholipids and lipopolysaccharides, and the cytoplasmic membrane has phospholipids bilayer in which essential proteins are embedded. Based upon the structural characteristics of cell wall and cell membrane, antimicrobial polymer agents are designed. Antimicrobial polymer agents must have cationic hydrophilic and hydrophobic macromolecular systems which will be major target site for which the cytoplasmic

Table 15.1 Polymer medical device applications.

Polymer type	Medical device applications
Polyethylene	Orthopedic implants, containers, catheters, non-woven textiles
Polypropylene	Disposable items (e.g., syringes), non-woven textiles, membranes, sutures
Polyurethanes	Films, tubing, catheters
Polyvinylchloride	Catheters, tubing
Polyamides	Sutures, packaging, dental implants
Polyethylene terephthalate	Sutures, artificial vascular grafts

membrane will behave as active agents. These polymers which have a polar functional group will block membrane that bear cationic charge and a hydrocarbon functional group that are non-polar hydrophobic in nature block (or hydrophobic structure of a whole link), or random copolymers formed by a hydrophobic monomer and a hydrophilic co-monomer interactions with a functional group. Such polymers and copolymers structures has high affinity to bind with bacterial cell due to lipophilicity to cause the damage of structure and integrity of bacterial cell membrane which may cause the leakage of cytoplasmic content, cell lysis, and cell membrane disruption [8, 9].

15.2.1 Passive Action

A passive polymer layer prevents the attachment of bacteria by decreasing the adsorption of protein on surfaces. They repel the bacteria and they do not kill or interact with bacteria. Microbial membrane has hydrophobic character and negatively charged molecules then passive polymers may be hydrophilic, negatively charged, and low surface free energy [10, 11]. The mechanism of passive polymer is shown in Figure 15.1. Passive polymers are made up of the following. a) Surfaces that are self-healing and slippery in nature are mostly liquid infused highly porous surface, for example, poly(dimethyl siloxane). b) The polymers that have no charge include poly ethylene glycol and c) charged zwitterionic and polyampholytes polymers such as phospholipid polymers and phosphobetaine [1, 12]. Table 15.2 shows the example of antimicrobial polymers performing passive action.

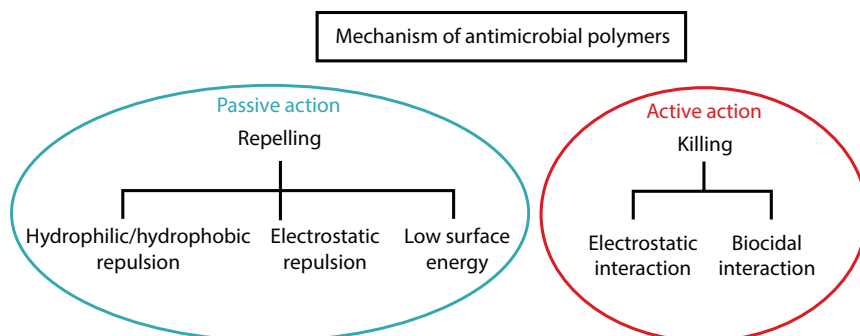


Figure 15.1 Schematic representation of mechanism of action of polymers.

Table 15.2 Polymers performing the passive action.

Polymer	Target	Remark	Reference
Poly[3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate- <i>b</i> -2-(diisopropylamino) ethyl methacrylate]	<i>Staphylococcus aureus</i>	Zwitterionic coronae and pH-responsive cores can impart bacterial anti-adhesive properties	[10]
Poly(2-methyl-2-oxazoline)	<i>Escherichia coli</i>	Dual-functional antimicrobial surface of poly(L-lysine)-graft-poly(2-methyl-2-oxazoline)-quarternary ammonium	[11]
Albumin, whey	<i>Bacillus subtilis</i> , <i>Escherichia coli</i>	No bacterial growth was observed on albumin-glycerol and whey-glycerol after 24 h inoculation	[12]

15.2.2 Active Action

Active polymers are capable to kill the microbes that stick to the surface of polymer. These polymers have the active agents which may be antimicrobial peptides, some cationic biocides, or other antibiotics that have ability to kill the bacteria when they are come into direct contact. The polymers kill the microbes by which mechanism depends upon the active agent present in the polymers. The mostly active antimicrobial polymers are usually activated with the positive charged specie such as quaternary ammonium, it may interact with the components of cell wall of bacteria and eventually cause the destruction of the cytoplasmic membrane of microbes, due to this destruction results, leakage of intracellular components takes place and consequently cell death occurs [1, 11]. There are polymers such as polyguanidine, polyethylenimine, and *N*-halamine that have capability to exhibit the antimicrobial activity. Polyethylenimine can cause the rupture of the cell membrane of bacteria by the development of electrostatic force of attraction between the polymer polyethylenimine and cell membrane of bacterial. Polyguanidine polymer has capability to inhibit the bacterial growth by the adhesion with cell membrane and subsequently destruction of Ca^{2+} salt bridges occur and eventually death of cell takes place. *N*-halamine can cause inhibition of cell growth and also responsible for inactivation of membrane due to presence of halogen group have oxidative effect which target such as thio and amino groups present in the receptors of cell [4]. Table 15.3 has the list of active polymers and applications of these antimicrobial polymers, showing that most of newly developed antimicrobials polymers are usually based upon quaternary ammonium group may be inform of salts.

15.3 Factor Affecting Activity of Antimicrobial

15.3.1 Polymers

There are many factors that have strong effect on the antimicrobial activities of the polymer such as molecular weight, charge density, hydrophilicity, counter ions, and pH.

15.3.2 Molecular Weight

Molecular weight has significant role in physicochemical characteristics of polymers. The molecular weight is an important factor for controlling

Table 15.3 Passive polymers perform antimicrobial activity.

Polymer	Target	Antimicrobial substance	Remark	Reference
Nisin-immobilized ozorganosilicon	<i>Bacillus subtilis</i>	Nisin	Superior antimicrobial activity, and resistant to several cleaning conditions	Yu, K., <i>et al.</i> [13]
Polyurethane containing quaternary ammonium	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i>	Quaternary ammonium	Good antimicrobial activities against even at low concentrations (5 wt %)	[14]
Poly(<i>n,n</i> -diethylethylenediamine-co-yrosol-based acrylic)	<i>Staphylococcus epidermidis</i> , <i>Staphylococcus aureus</i>	Tertiary amine	Combination of two active compounds provide a synergistic action against biofilms and suppress reactive species oxygen	[15]

biocidal activity especially for the polymethyl acrylates and polyacrylates with biguanides group in side chain [4]. The molecular weight of polymer between 5×10^4 and 1.2×10^5 Da is optimal for the performing biocidal action. The antimicrobial properties increase with decrease the molecular weight from 5×10^4 Da while activity of antimicrobial polymer decrease with increase the molecular weight from 1.2×10^5 Da. The antimicrobial properties depend upon the permeability of polymer through the cell wall [8].

Gram-negative bacteria has greater diffusion rates for many antimicrobial polymers due to composition of cell wall but Gram-positive bacteria possess low diffusion rates [8]. In the case of ϵ -PL, alkyl chain length produces modifications. These have significant effects on the microbial activity and L-lysine chain length of residues that is present in the polymer having the optimum activity for the inhibition of growth of microbes [4].

15.3.3 Charge Density

Polymers have high positive charge clouds; they can develop the strong electrostatic force of interaction with cells of bacteria. In chitosan, charge density of polymer increase due to increasing of degree of deacetylation (DD), due to which electrostatic force of attraction increases as a result antimicrobial activity enhance [4]. At a higher rate of deacetylation, chitosan has higher antibacterial activity against *S. aureus* [13]. The polymers that have high charge density such as asparagine N-conjugated which is incorporated into chitosan structure for enhancing the antimicrobial action of polymer [14]. Chitosan structure is modified into guanidinylated chitosan which exhibit the higher antimicrobial action [15]. While chitosan having *N*-carboxyethyl can exhibit the antimicrobial action because of lack of free amino group [16].

15.3.4 Hydrophilicity

Hydrophilicity is a very essential factor for actions of antimicrobial agents [4]. Derivatives of water soluble chitosan that can be synthesized by the process of alkylation, acylation, quaternization, saccharization, and metalization show the higher antimicrobial activity [17].

15.3.5 Counter Ions

The quaternary ammonium/phosphonium compounds have counter ion effect. Counter ions which have high affinity towards quaternary

compounds have lower antimicrobial action because of slow release of the free ions present in the medium. For quaternary ammonium compounds, chloride and bromide exhibit the high antimicrobial activity [4].

15.3.6 pH

The effect of pH on chitosan and antimicrobial polymers which are amphoteric in nature has been studied. Chitosan shows antimicrobial action depending upon its pH. Antimicrobial action of chitosan is limited to acidic environment because it dissolves in water only in the acidic conditions by such mechanism in which protonation of the amino group takes place. The antimicrobial activity and solubility of chitosan is increased over the entire range of pH by incorporating quaternary ammonium salts in chitosan backbone [18].

15.4 Medical Applications

The newly developed antimicrobial agents have the broad spectrum against the pathogens and also responsible for modulated immune responses [19–23]. The wound-dressings having antimicrobial agents are usually consist of cotton gauze and antimicrobial peptides for antimicrobial activity. These are combine with polyanion(sodium alginate) and polycation (chitosan) that show high antimicrobial activity towards *Klebsiella pneumonia* and *Staphylococcus aureus*. These types of wound dressings have also been proved as non-cytotoxic to the dermal fibroblasts of human [24]. The urinary tract infections associated with the use of catheter is the common reason for hospital-acquired infections. Urinary catheters impregnated with a mixture of triclosan, sparfloxacin, and rifampicin have been designed. The newly developed silicone catheters release the drugs about one month generally. The novel antimicrobial catheters can inhibit the colonization and adhesion of *Escherichia coli*, *Staphylococcus aureus*, and *Proteus mirabilis* approximately for a period of 7–12 weeks [25].

15.5 Conclusion

Recent advances show that antimicrobial polymers have gained the high attention in both industrial and academic research fields. This mini-review summarizes the mechanism of actions of polymers and factors that

affecting the action of polymers. Recent advances made in antimicrobial polymers have been discussed. Passive antimicrobial polymers prevent the bacterial adhesion and growth of microorganisms that is alternative strategy rather than killing the microbes directly with active antimicrobial polymers agents. Despite of the recent advances in antimicrobial polymer substances, there is a need for the further classification of antimicrobial polymers depending upon their antimicrobial mechanism of action on the microbes. Biofilm-associated mechanisms especially require a very intensive effort for designing of new antimicrobial substances. The highly effective antimicrobial polymers can be formulated by the combination of different kinds of antimicrobial polymers having the different mechanism for exhibiting the antimicrobial activity. The more challenges in this field for the development polymers can exhibit their actions for the long period of time and have broad spectrum for antimicrobial activity. The major demand is that delivery of the drug on the desired site in a very controlled manner and for longer period.

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Characterization Techniques for Polymer Coatings

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Abstract

Polymer coating is a process of coating polymeric material to the external surface of dosage forms with certain intentions including protecting the active pharmaceutical ingredient (API) against the environmental hazards or against the body fluids, protecting body from adverse effects of API and modifying the release of API. In this respect, different coating types as film coating, enteric coating, extended release coating, and organic-inorganic nano-composites hybrid coatings are being used in pharmaceutical industry. Spray coating is a widely used technique for polymer coating. Irrespective to the reasons and types of polymer coating to the dosage forms, polymer films need evaluations for certain properties. This chapter has a collective knowledge about polymers, their coating technique, types of coating, and characterization techniques which include water vapor permeability, oxygen permeability, thermal characteristics, and mechanical and adhesive characteristics of the polymeric materials used for coating.

Keywords: Polymer coating, technique for coating, types of coating, film coating, extended release coating, water vapor permeability

16.1 Introduction

Polymer is derived from two Greek words, poly means many and mer means part. It is composed of monomers, the building blocks of polymer.

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According to the definition of IUPAC, a polymer is a substance composed of macromolecules. A macromolecule is a molecule of relatively higher molecular mass, the structure of which is comprised of many repeating units called monomers derived from molecules of relatively lower molecular mass [1]. Polymers have some unique characteristics including low density, good corrosion resistance, low coefficient of friction, good mould ability, low mechanical properties, poor tensile strength, and poor temperature resistance [2]. Many synthetic and natural polymers are extensively used as pharmaceutical excipients and for coating on the solid oral dosage forms as they mask some undesired physicochemical properties of drugs and hence improve the therapeutic effect. They allow increased solubility, swallowability, biodegradability, pH dependency, advanced coatings, and inhibition of crystallization [3].

Polymers can be classified in various aspects, as based on source, polymers may be natural, semisynthetic, or synthetic, and on the bases of structure, they may be linear, branched chain, or cross linked. Polymers have extensive applications in the field of pharmaceutical sciences as binders, disintegrating agents, and coating materials in the manufacturing of tablet, gelatin manufacturing in capsules, as suspending agents in suspensions, as emulsifying agents in emulsions, as film coating to mask bitter taste and modify drug release characteristics and in the drug delivery of various contraceptives and hormones [4].

16.2 Polymer Coating

Coating is a process of coating material (polymers) to the external surface of drug dosage form to achieve certain benefits and properties of the API as compared to uncoated variety, the benefits may include protection of API against the environmental hazards, protection against the harsh environment of the GIT or body fluids, protection of body itself against the adverse effects of API, or modification of the release characteristics of API [5]. Components for coating include polymers, pigments, plasticizers, opacifiers, glidants, binders, anti-tacking agents, surfactants, fillers, and extenders whereby polymer constitutes a major component. Important polymers used for coating are hydroxypropylmethylcellulose (HPMC), polyvinyl alcohol (PVC), sodium alginate, cellulose acetate phthalate, methacrylic acid co-polymers, etc [6].

Polymer coating has profound merits including (a) protection against environmental factors like temperature, sunlight (UV light), moisture, and toxic gases, (b) facilitation of swallowing, (c) mask unpleasant taste and

odor, (d) improved appearance, (e) facilitate product identification during manufacture and packaging, (f) provide immediate release, sustained release, specific release, controlled release or targeted release of drug, and (g) improve mechanical strength of the dosage forms [6]. But coating may have some demerits like increase thickness and weight of tablets, increase cost of formulation, impact on surface smoothness due to uneven coating, altered pharmacodynamics of the API, sticking and picking, orange peel effect and bridging, i.e., inadequate spreading of coating solution [6, 7].

16.3 Technique for Coating

Spray coating is the most preferable technique for coating process which involves the formation of fine droplets of the coating solution, and then, this solution is deposited and coalesced on the surface of the substrate. Through the technique of atomization in spraying nozzle, the liquid which is used for coating is broken. Then, these droplets are deposited on the substrate from where they undergo coalescence to form a film [8].

Currently, ultrasonic atomization technique is preferably employed for the coating procedure which utilizes high frequency sound vibrations to form a fine mist of the coating solution. The benefits of spray coating include good transfer efficiency, simple and economical, good reproducibility and uniform coating on both planar and non-planar surfaces, and formation of tiny droplets which are in the micrometer range. Spray coating is dependent on some material and process parameters including (a) polymer solution's concentration, (b) solvent employed, (c) the drug and its dosage form, (d) flow rate of polymer solution, (e) temperature, (f) the distance between the spraying nozzle and the dosage form, (g) the speed of the moving nozzle, and (h) air pressure of the nozzle [9].

16.4 Types of Coating

16.4.1 Film Coating

It is a process of deposition of a thin polymeric film onto the solid dosage forms like tablets, capsules, or pellets [6]. Film formation of polymer coatings is very important with respect to the purpose of coatings of drugs like enteric resistance or modified release [10]. There may be free film or applied film. Casting method is generally used to obtain free films in which

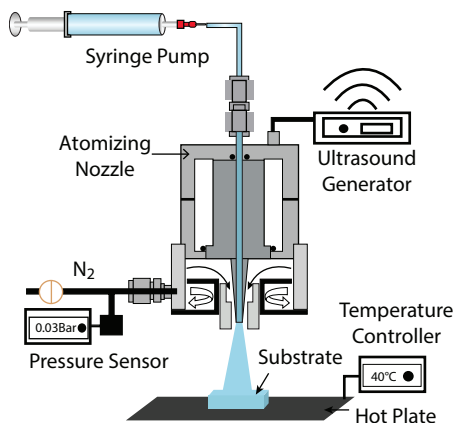


Figure 16.1 A schematic representation of apparatus used for spray coating. Adopted from Ref. [9].

the solution or dispersion of polymeric material is applied onto the substrate, and then, solvent is evaporated. A spray atomization technique is used for this purpose to avoid uneven film surface. But in case of applied film variable substrate, processing parameters, storage conditions, and coating formulations are required [11] Figure 16.1.

Film coating can be achieved using organic polymer solution or aqueous polymer dispersion [10]. While using organic polymer solution, after deposition, the dissolved polymer forms the film on the surface of the dosage form by undergoing sol to gel transition. When the organic solvent is evaporated, then the molecules of polymer come closer to each other and form a homogenous film with high penetration of polymer chain. Low polymer concentration and toxicity of the solvent which requires its recovery are the drawbacks of using organic polymer solution [10, 12].

To address these drawbacks, aqueous polymer dispersions are preferred in which the film is formed by the coalescence of the polymer molecules after the evaporation of water. This process is generally divided into three phases. In 1st phase, water evaporation occurs, and then, concentration of the dispersion is increased until dispersed particles form a closed-packed array. In 2nd phase, temperature is increased above the minimum film formation temperature (MFFT), and then, particles undergo deformation making polyhedral structures. In the last phase, the temperature is further increased above glass transition temperature (T_g) which leads to the inter-diffusion of polymer chains forming a continuous film without the distinguishable particles [10]. Here, the temperature plays an important role on the polymer diffusion rate and film formation [13].

16.4.2 Extended Release Coating

Extended release polymeric coating offers numerous advantages including controlled release of the therapeutics having short half-lives, inhibiting the non-specific distribution of drug and hence lowering the toxicities [14]. Extended release polymers are coated either by aqueous polymer dispersions or organic polymer solutions. Organic systems have some environmental and toxicological hazards whereas high temperature, high energy, and long processing time are the drawbacks of aqueous systems. In aqueous dispersion, high energy input is required to evaporate the dispersion medium. Moreover, less amount of coating material is dispersed in the large amount of dispersion medium which is then needed to be evaporated [5]. Films formed from aqueous dispersions undergo aging phenomena also. To address all these drawbacks, dry powder coating is used which does not use organic solvent and limited water is used. It is a time-saving process [10].

In dry coating, polymeric material is cast as a micronized powder directly onto the surface of dosage form with or without the spraying of liquid plasticizer [15]. Dry coating process occurs in two phases. The 1st phase is the coating phase in which the dry powder mixture of the polymeric material and plasticizer is applied to the substrates, whereas in 2nd phase known as curing phase, a film is formed onto the substrate [5].

16.4.3 Organic-Inorganic Nanocomposites Hybrid Coating

These coatings are nano-phase separated metal-oxo clusters which are connected to a continuous organic network of polymers through a phase coupling agent. Resistance to abrasion and scratching, heat stability, and improved mechanical properties are the merits of this coating technique. These hybrid materials are obtained by *in situ* sol-gel process in which silica domains are embedded into polymer network. Hydrolysable multifunctional alkoxy silane is used as precursor for the formation of inorganic domains which then undergoes a series of hydrolysis and condensation reactions. A suitable coupling agent is used to achieve an interconnected network without macroscopic phase separation; it provides bonding interactions between the organic phase and inorganic phases [16].

Currently, this coating technique is carried out by combining sol-gel process with a photo-polymerization process, which has advantages of both curing methods. In this technique, the formation of polymer is hastened through fast transformation of the liquid particles into a solid film [17]. As it is a solvent free process and carried out at the room temperature,

so this technique is environment friendly and hence becoming increasingly important for coating [16].

16.4.4 Enteric Coating

Enteric coating allows release of API in the lower part of small intestine to protect it from the harsh acidic environment of stomach. It involves the use of biodegradable polymers such as azopolymer, dextrans, pectins, amylose, etc., as coatings in oral formulations [18].

16.5 Characterization of Coating System

16.5.1 Water Vapor Permeability

It is a parameter to assess the effectiveness of film coating against water. Various factors have an impact on water vapor permeability like film thickness, film composition, and technique employed for the film preparation. Fick's first and Henry's laws are utilized to access the water vapor permeability. Figure 16.2 is the schematic representation to assess water vapor permeability for free films. The containers shown are of glass or aluminum containing saturated solution of salt. The sample film is placed over the opening of container. Transmission cells are kept in desiccator whose humidity is known by creating a difference in water vapor pressure. By measuring weight change of the transmission cell over time, a graph is plotted between the weight change and time. From the slope of the line which is calculated by line of regression, the value of water vapor transmission rate (WVTR) is obtained [11].

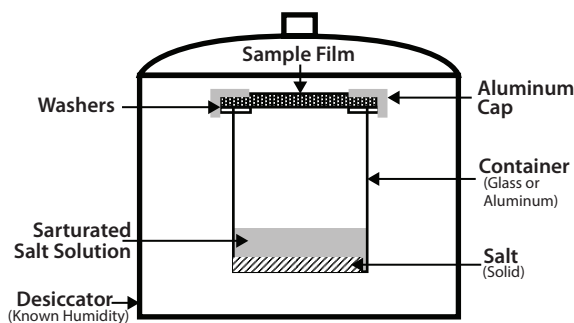


Figure 16.2 Schematic representation of assessment of water vapor permeability for free film. Adopted from Ref. [11].

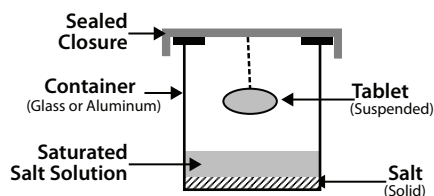


Figure 16.3 A schematic representation of assessment of water vapor permeability for applied films. Adopted from Ref. [11].

For applied films, the transmission cell apparatus for free film is modified. As shown in Figure 16.3, a wire loop is suspended over the saturated salt solution in a closed container made up glass or aluminum. The coated tablet under analysis is placed on that wire loop. The weight of tablet is calculated over time and a graph is plotted. From the slope of line, the value of WVTR is then determined [11].

16.5.2 Oxygen Permeability

After water vapor permeability, oxygen permeability is the most commonly studied parameter. This parameter is important for the drugs which are affected by oxidation. Oxygen permeability is actually the measurement of effectiveness of the coating polymeric material against oxygen and it is affected by film thickness and film composition. For free films as shown in Figure 16.4, test film is placed between the two chambers: inside chamber and outside chamber. Nitrogen gas is eliminated from the both chambers. Pure oxygen is passed through the one side of chamber and then using a coulometric sensor, diffused molecular oxygen is quantified [11]. For applied films, nondestructive paramagnetic

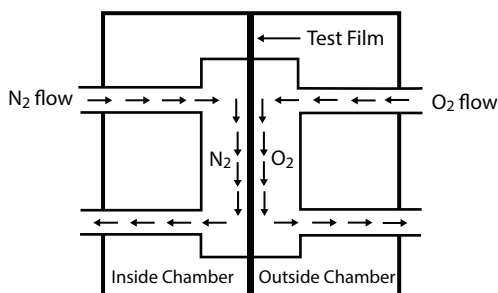


Figure 16.4 Schematic to quantify oxygen permeation for free films. Adopted from Ref. [11].

resonance spectroscopic technique is used in which lithium phthalocyanine crystal is inserted into the dosage form and then partial oxygen pressure (pO_2) is determined. A graph is plotted between pO_2 and time and then slope is calculated using line of regression which indicates oxygen permeation [11, 19].

16.5.3 Thermal Properties

16.5.3.1 Glass Transition Temperature (T_g)

T_g is the macro-manifestation of polymer chain's flexibility, an important parameter in case of amorphous polymer. It is defined as the range of temperature in which a polymer changes from rigid to soft material [20]. If temperature is less than T_g , the movement of polymer chain is restricted and a rigid film is formed and if temperature is increased above T_g , then the mobility of polymer chains is increased and crystallization of polymers is enhanced. T_g is measured through differential scanning calorimeter (DSC) [21]. DSC is a type of thermo-analytical technique that determines the heat and temperature flow either absorbed or released associated with the sample as a function of temperature and time [22]. In this technique, the sample pan containing polymeric material and reference pan which is kept empty are heated at the same rate simultaneously and the thermal transitions at which more energy is absorbed or released are determined. DSC is also used to detect polymorphism, determine melting temperature, evaluate polymer miscibility, and study oxygen degradation [11].

16.5.3.2 Minimum Film Forming Temperature (MFFT)

MFFT is the very important parameter for the film formation. It is defined as the minimum temperature at which a cast film becomes crackless or clear leading to coalescence of polymer which is applied to a substrate into a thin film [12, 23]. If temperature is less than MFFT, then a white opaque layer is formed or powdery material is appeared on the surface of the substrate but if temperature is equal to or higher than MFFT, a transparent film is formed. Hence, in the coating process, bed temperature should be above the MFFT. For the determination of MFFT, a temperature gradient plate is employed with drying air blown. The polymeric material is placed onto that plate and drying air is then passed through the sample. The lowest temperature at which a clear and transparent film is formed is inspected visually and this temperature is considered as the MFFT of that

polymeric material [11, 21]. The value of MFFT is affected many factors such as presence of plasticizers or other excipients in the polymeric material [21].

16.5.4 Mechanical Testing

Polymer films must be mechanically strong enough so that they do not undergo breakage or fracture while processing, manufacturing, packaging, transportation, or storage. For this purpose, tensile strength, stress analysis, compression testing, puncture strength, and dynamic mechanical analysis are performed to evaluate the mechanical properties of polymeric material used for coating [11].

16.5.5 Polymer Adhesion

Poor adhesion between polymer and substrate may cause flaking or peeling effect and moisture can accumulate at the interface of film and substrate which can affect stability of drug and also the mechanical strength of the polymeric film. Polymer adhesion is related to both the internal stresses within the polymeric film and the interactions between the film and substrate. Strength of interfacial bond and the internal stresses within the polymeric film are the important factors which affect polymeric adhesion [24]. Several methods are employed to assess the polymer adhesion with the drug dosage forms. In peel test, a modified tensile tester is utilized. It peels the film from the surface of a tablet at an angle of 90° . Another methodology used is butt adhesion test (Figure 16.5) in which the whole film is removed from the surface of tablet. This method eliminates the variations

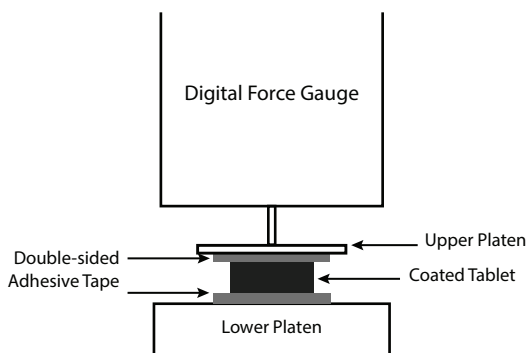


Figure 16.5 Schematic of butt adhesion test. Adopted from Ref. [11].

because of elasticity of film and is less affected by uniformity of tablets. This method utilizes flat faced tablets, but for concave tablets, a foam or rubber backing is added to ensure the uniform contact between the force gauge and film surface [11].

16.5.6 Surface Roughness

Rough surface of the coated tablet can influence drug release and it may affect the aesthetic appearance. Electron microscopy technique is employed to predict the qualitative analysis of surface morphology, whereas for quantitative analysis, profilometry is employed in which a sensing head is used which moves across the substrate. Atomic force microscopy is another quantitative method in which a sensor examines the small areas on substrate [11].

16.5.7 Film Thickness and Uniformity

Several approaches are applied to check film thickness and uniformity. Microscopic method can be used but it is tedious and time consuming. Another method is laser-induced breakdown spectroscopy, an elemental analysis technique, which is based on detection of atomic emission from a polymeric material. Computer-aided tomography (CAT) is a medical imaging technique which is now widely used. This involves the transmission of x-rays onto the sample, and then, the intensity of the transmitted x-rays is measured using a detector [11].

16.6 Conclusion

Polymer coating plays a key role in the drug design and modified drug delivery systems. This mini-review throws light on the type and properties of the polymeric materials and it also explains the characterization techniques that are needed to assess the mechanical and thermal properties of the polymers. All these techniques are required for the pharmacist or technician before coating processes and helps in the modification of drug release properties.

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Polymer Coatings for Corrosive Protection

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Abstract

Corrosion plays a predominant role in all the major industries that use corrosive materials mainly of chemical industries. Mainly, the corrosion may be controlled by adopting corrosion control methods. There are various types of corrosion control methods among those coating conductive polymers over the medium mainly generates corrosion resistance to the base material, which contains toxic and hazardous materials that damage the environment, to an extent. These major commitments have led the researchers for the development of innovative protective coating materials and methods which adopts carbon-based materials and conductive nanocomposites. Recent developments indicate that mainly the conductive polymers have increased the attention of the industrial and research community due to its economic viability and improved applications. Generally, polymers hold a long carbon linkage chain which therefore capable to block wider area of the metal surfaces over corrosion which is due to the adsorption property. The deposition of thin coating over the corrosive surface behaves as a barrier between both the metal surface and the environment for protecting such surfaces. This review article discusses various methods that are adopted for protecting metals from corrosion, mainly about nanomaterials, conducting polymers, nanocomposites, and also carbon-based materials for fighting against corrosion behavior.

Keywords: Metal substrate, corrosion, polymer coatings, conducting polymers

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17.1 Introduction

Corrosion control is a significant topic of growing concern in the electronic and metallurgical industries. Metal corrosion is one of the most significant issues in the global arena. The most common technique of corrosion prevention is to apply paint or organic layer to the substrate of metal. The organically coated materials can preferably provide corrosion resistance that lasts for longer time. Moreover, this advantage relies on the capacity of the coating to protect the covered metal layer when failures occur during its service life [1]. The most commonly used technique could be to carry out polymer coatings [2]. Conducting polymers as film developing corrosion substances or in a protective coating has attracted greater and greater attention owing to the excellent anti-corrosion capability and friendship with the environment [3]. The benefit of conducting polymers and their composite materials over other coatings, like paints, is that they do not produce environmental damaging. Furthermore, conducting polymers exist as both a physical barrier and an electronic barrier, improving the protection provided by other materials which act only as physical barriers [4].

The conducting polymers perform redox reactions and thus enable the bonding and removal of the counter ion (doping) in reaction to variations in the surface of metal potential caused through local electrochemical operations owing to corrosion. Doping, which could be incorporated or removed by conducting polymer based on local corrosive environment, is mostly a preventative inhibitor of local corrosion after discharge [5, 6]. This is one of the techniques described in the exploitation of the benefits given when a conducting polymer has been used as a primary ingredient of corrosion-resistant layer [7]. The use of conducting polymer for protecting metal from corrosion has drawn excellent concern significantly over the past 35 years. Despite the extensive work on anti-corrosive characteristics of conducting polymers, there are still many difficulties for conducting polymer-based coatings to meet the physical-electrochemical and mechanical demands of high-performance anti-corrosive coatings through a wide range of practical conditions. Disadvantages of conducting polymers as anticorrosive coatings are including (i) irretrievable usage of the load contained in the conducting polymer, which can oxidize the base metal as a result of creating passive oxide layer; (ii) anion-exchange characteristics; (iii) porous composition and bad barrier impact; and (iv) bad adherence to the parent metal.

In particular, all of the above-notified drawbacks are enlarged within extreme corrosion environment as it is in the existence of chlorides that

may enter the steel surface either because of permeability of the conducting polymer layer or because of its anion-exchange characteristics when chlorides replace the conducting polymer layer anions. One of the effective methods for eliminating the above drawbacks is to consider conducting polymer-based composite structures generally containing a conducting polymer in which metal oxides which are distinct inorganic fillers were embedded. These conducting polymer-based composite materials mix the redox characteristics and therefore the self-healing function of conducting polymer with inorganic filler characteristics. As a result, conducting polymer composites have exposed stronger mechanical as well as physico-chemical characteristics enhancing barrier effect, adhesion property, and possibly hydrophobic characteristics. Nanocomposite conducting polymer-based coatings appear to blend the characteristics of conducting polymers and organic polymers more effectively with those of inorganic metals [8, 9]. This chapter examines the implementation of conducting polymer-based coatings to prevent the corrosion of metals and alloys described in latest developments.

17.2 Basics of Corrosion

Corrosion is commonly occurring defect that can be defined as the deterioration or degradation of a particular substance and also the properties of the same which is usually metal by using it for a longer period of time due to the environmental disclosure [10, 11]. This is an exergonic cycle because the metal falls to the lowest possible state of heat. So the materials like steel and aluminum have a general capacity to reform into lower state of energy when exposed with water and oxygen to form iron and aluminum oxides. These corroded materials are the final processed metals that degrade over a period of time when exposed to environment. Thus, the cycle of the industrial products from its processed ores and or its original state is indicated in Figure 17.1 with the consideration of both environment and materials.

Identifying these two elements can evaluate effective strategies to counteract these destructive processes. The metal corrosion is broadly classified into three groups.

- Wet oxidation in a corrosive atmosphere of dissolved bacteria, the electrolyte is usually a solvent and the process which is electrochemical.

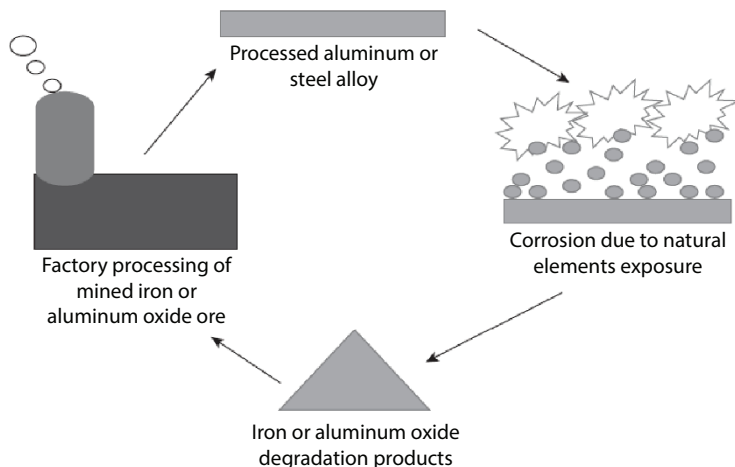


Figure 17.1 Schematic representation of the corrosion cycle of metal alloy [11].

- In other liquids such as fused salts and/or fused metals, oxidation.
- Dry corrosion where high-temperature gas in dry condition is the corrosive condition.

The wet corrosion behavior is extensively discussed in this article which mainly discusses the wet corrosion processes which affect the metals and its alloys and also the techniques that exist for controlling the corrosion behavior and also its effects.

Corrosion is mainly categorized into three groups, *viz.*,

- Group I - Nature of corrodent,
- Group II - Appearance of metal that is corroded, and
- Group III - Mechanism of corrosion.

Group I is generally intended as wet or dry condition, where wet corrosion occurs in liquid medium usually water which means freshwater or saline. The aqueous generally termed as wet corrosion process comprises three most essential elements that are required for the corrosion process to happen which are cathodic reaction, anodic reaction, and electrolyte solution. Group II implies that how the corrosion takes place through electrochemical or through direct chemical reaction. When referred to Group III, it describes which type of corrosion affects the metals which may be

uniform corrosion, corrosion over the entire surface or in only small areas that affect the corrosion process generally called localized corrosion.

17.2.1 Essentials of Corrosion

The metal's anodic reaction and oxidation result in metal breakdown, which is transferred as M^{n+} ions. Also, the cathodic reaction engrosses oxygen. Reducing the oxygen content is mostly predominant cathodic reaction in natural environments such as freshwater, seawater, atmosphere, and soil. This method forms electrical circuit devoid and charges accumulation. The anodic releases electrons that further got inducted through metal to the cathode which in turn is consumed by the cathodic reaction. This process requires an ionically conducting liquid that should be in contact with metal. The ion conduction through the electrolyte closes the electrochemical circuit, also all the three elements should be present for wet corrosion to take place. Normally M^{n+} ions are conducted towards OH^- ions and when both these gathered produce a metal hydroxide that gets deposited on the metal surface. Copper and iron metals also follow similar trend of corrosion process where water is used as an electrolyte in the presence of dissolved oxygen (Figure 17.2).

As depicted in Figure 17.2, the two main features that is the source of corrosion are the oxygen and electrolyte. When hydroxide gets deposited onto the metal surface, there may be a reduction of oxygen available for continuation of corrosion process. This continuous metal hydroxide layer reduces oxygen reduction reaction which in-turn reduces corrosion rate. Because when metal dissolution or oxygen reduction rates are equal, the reduction in any of these will result in decrease in other. Here, the rate of corrosion is considered under cathodic control. This is one

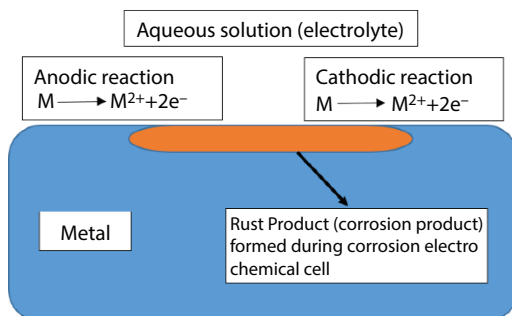


Figure 17.2 Anodic and cathodic reaction.

of the widely adopted methods for controlling corrosion by nature. This approach is commonly used in the design and management of corrosion naturally. In many cases, the corrosion products form a continuous layer of oxides that are similar to crystallographic composition. The generated films through this process prevent conduction of metal ions. The corrosion rate was very slow as the corrosion rate is under anodic control. This is called as passivation and is occurred for materials like aluminium and steel under natural conditions.

17.2.2 Methods of Coatings

Although the variation in pre-treatment and coating development is almost limitless, instances of popular methods used by paint coatings for corrosion control of steel substrates are explained below.

17.2.2.1 Zinc-Rich Coating

Generally, this zinc-rich coating comprises zinc ions and thus, by a sacrificial mechanism or cathodic protection, protects the steel. These layers must comprise 85%–95% w/w of zinc in order to have adequate electrical contact with the metal. Furthermore, the subsequent zinc corrosion components, which shape selectively when exposed to atmosphere, that intends to block pores in the coating which further enhances the coating's resistance characteristics. Furthermore, through this method, mainly two techniques of corrosion protection, sacrificial abided by enhanced resistance characteristics as the zinc is consumed.

17.2.2.2 Inhibitive Coating

Usually utilized as primers, inhibitive coatings are acquired by incorporating pigments which discharge materials that inhibit corrosion. The content of moisture consumed by the coated material helps the pigments to react and passive the steel. The overall efficient inhibitors like strontium chromates, indeed, have hazardous impacts over the environment. Because leaching is the basis for the discharge of inhibitors, coatings are to be extremely pigmented ensure adequate corrosion. Hence, the harmful substances were consistently discharged into atmosphere even if this is not required.

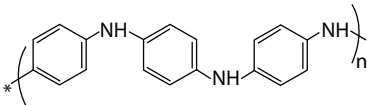
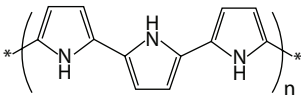
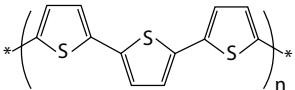
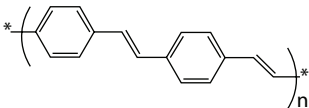
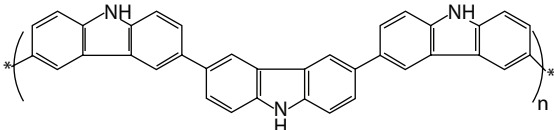
To summarize, paint coatings are important to prevent corrosion of steel materials and the requirement for environmentally friendly and non-toxic formulations to substitute standard paint content. Lately, the uses of polymers-based conducting material have demonstrated this promise

[7, 12–15]. The eco-friendly aspect of conducting polymers together the redox and strength characteristics leaves them excellent coating materials to protect metal alloys against corrosion.

17.3 Conducting Polymer-Based Coatings for Protection Against Corrosion

There are several conducting polymers accessible in commercial form. These generally include polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), and others like polythiophene, polyindole, polyrhodanine, poly(phenylenediamine), and poly(carbazole) [16–22]. The synthesis of conducting polymers is based on chemical or electrochemical oxidation techniques [23, 24]. Conducting polymers have discovered their applications in the sector of metal and metal alloy corrosion protection since the 1980s. Table 17.1 shows the chemical structure of conducting polymers.

Table 17.1 Chemical structure and conductivity of widely used for metal protection.

Conducting polymers	Chemical structure
Polyaniline (PANI)	
Polypyrrole (PAN)	
Polythiophene (PTh)	
Poly(para-phenylene vinylene) (PPV)	
Polycarbazole (PCz)	

Their convenience of synthesis combined with electrical conductivity via both chemical and electrochemical techniques allows them for utilizing as anti-corrosive materials. Many different interaction processes can be used to perform conducting polymers on a variety of substrates. These processes depend on kind of substrate that is utilized, the use of particular conductive polymers, physical characteristics, its chemical composition, the quantity and type of dopant are using, the quantity of conductive polymer utilized, and its relative percentage to other active ingredients that are used for coating. The preparation of surface also has a significant impact on the conductive polymer functional characteristics. This becomes more essential when, under the layer, there are problems associated with the adhesion and development of potential corrosion products. The local area's exposed environment and pH also have a tremendous impact on these polymers performance as coatings. A conducting polymer can be used either as a primer coating on its own or used as a primary coating together with traditional base coat, or otherwise, the same could be mixed with polymer coatings or utilized as an anti-corrosive material for coating formulation. The above methods are discussed in the previous research under the category of different conducting polymers.

17.3.1 Chemical Oxidative Polymerization Technique

This method is widely used for the preparation of conducting polymer-based coatings as it is most simple way to produce large-scale conducting polymers. In the event of using conducting polymer as primers, drawbacks of chemical polymerization are as follows: the restricted solubility of conducting polymers, and particularly of PANI, in most prevalent organic-based solvents and the low adhesion between conducting polymers and steel substrates. For example, in almost all common solvents, PANI, the widely used conducting polymer in various applications, is generally insoluble, and numerous techniques are often utilized to enhance PANI process ability and solubility [25].

The existence of immobilized dopants in the polymer chain, such as sulfonic groups, improves the solubility of polar solvents [26]. Suitable binders are frequently used to enhance the adhesion of the PANI-based layer to metal substrates. A suitable oxidant initiator substitutes the enforced capacity needed in electrochemical polymerization in the event of chemical oxidative polymerization. Table 17.2 shows a range of such oxidants used with their standard oxidation potential for conducting polymer chemical synthesis, E0.

Table 17.2 Oxidants and their standard oxidation potential, E^0 , used by chemical polymerization for conducting polymer synthesis [25].

Oxidant	$E^0(V_{SCE})^a$
H_2O_2	1.538
$(NH_4)_2S_2O_8$	1.698
$Ce(SO_4)_2$	1.478
KIO_3	0.848
$FeCl_3$	0.528
$K_2Cr_2O_7$	0.988

Behind chemical oxidative polymerization, many different types of synthetic routes exist, such as catalytic enzyme polymerization, interfacial polymerization, and emulsion polymerization, widely used in the design of conducting polymer morphologies and characteristics need for particular applications. While the number of conducting polymer-based protecting coatings studies are dominated through the preparing of composition with primary components PANI, PTh, PPy, and its derivatives, some other conducting polymers have also been utilized against prevention of metal corrosion, like poly (para-phenylene-vinylene) (PPV) variants through a precursor technique [27], which varies from those of the earlier listed conducting polymers.

17.3.2 Electro-Chemical Oxidative Polymerization Technique

This polymerization process is regarded to be the significant technique of preparing homogeneous films of conducting polymer for desired coating film thickness and also surface morphology adhering to a metal electrode or semiconductive. Over the past few years, this electrochemical polymerization has drawn significant attention in the development of several conducting polymer nanostructures [28, 29].

Electrochemical polymerization offers different benefits relative to chemical polymerization: (1) increased bonding with metal substrate, (2) instantaneous doping with required doping anion, that is often selected as anion of supporting electrolyte in polymerization blend,

(3) fast polymerization at room temperature, (4) regulate of film thickness and possibly morphology and molecular structure, and (5) prevention of solubility complications encountered on metal substrates with several chemically synthesized conducting polymers. The disadvantages of electrochemical polymerization occur where polymerization on oxidizable metals are needed from acidic alternatives (e.g., polyaniline processing), as metal electro-dissolution can happen, and second when electrode position on huge substrates like buildings, pipelines, and boats are needed. Formerly, it is indeed unwieldy and practically inconceivable to electrochemically polymerize. Chemical deposition is preferable in these instances in combination with other methods such as casting and mixing.

Electrochemical polymerization could be deposited, potentiostatically or galvanostatically, using cyclic voltammetry (cyclic potential sweep). Figure 17.3 shows a typical 3-electrode cell used in electrochemical polymerization. The three electrodes, namely, reference electrode (RE), working electrode (WE), and counter electrodes (CE), are properly associated with a potentiostat/galvanostat processes reported by Bard & Faulkner *et al.* [30]. It is also possible to use an electrode cell of two numbers compatible with work and counter electrodes.

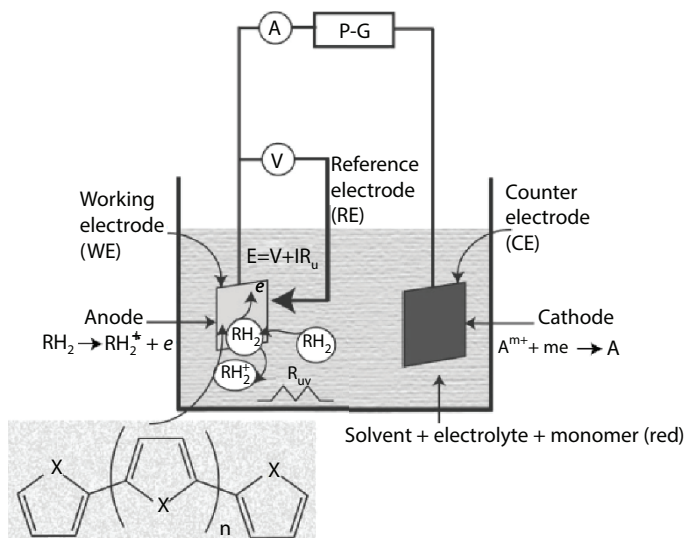


Figure 17.3 Typical 3-electrode cell used for electrochemical polymerization [32].

17.4 Synthesis of Conducting Polymer Commonly Used in Protection Against Corrosion

17.4.1 Synthesis of Conducting Polymer: PANI

PANI is indeed a conductive polymer belonging to the polymer class of semi-flexible rods. It has a p-type coupled spine group which allows electronic transmission while the polymer is partly corroded and protonated to the emerald state. The PANI most stable state is the emerald state. When PANI is completely lowered or oxidized, both pernigraniline and leucoemeraldine are similarly stable [31]. Manufacturing of printed circuit boards, electrostatic discharge coatings and also corrosion prevention are the major fields of application [32]. In PANI synthesis, two techniques are commonly used: chemical and electrochemical monomer polymerization in a suitable electrolyte. Chemical synthesis technique has to do with monomer oxidation by utilizing acid or alkaline intermediate oxidizing agent. Ammonium peroxydisulphate [33], ammonium persulphate [34], $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in HCl [35], H_2SO_4 solution [36], etc., are frequently used oxidizing substances. The acidic medium's pH level is often held between 0 and 2 while the alkaline medium pH is maintained as 4 [31]. Moreover, the use of chemical techniques loses patronage, because the technique is dreary and the synthesized substance can be contaminated.

The electrochemical method includes monomer oxidative polymerization of aqueous solution like LiClO_4 containing acetonitrile [37], salicylate solution [38], tosylic acid solution [39], H_2SO_4 solution [40], and oxalic acid [41], etc. The technique of electrochemical synthesis has the benefit of being a one-step technique that effectively controls the polymer chemical and physical characteristics. Also, it is not necessary to extract the product produced from this method from the extraction scheme (solvent mixture, oxidant, monomer), thus avoiding contamination. Electropolymerization on distinct kinds of steel and other metals in which passivation easily precedes the polymerization method was carried out from distinct organic and inorganic acid environments arising in disciple PANI coatings with adequate protecting characteristics in corrosion environments [42, 43].

PANI is used in practice for reinforcement of concrete steel bars. Saravanan *et al.* [44] investigated the epoxy primary for steel bars comprising PANI. Based on the existence of PANI in the layer, it was discovered in this study that the base metal repassivates. Epoxy PANI coating shows a greater incidence of chloride, which in the steel bar is one of the main symptoms of concrete corrosion. This was assessed by augmented investigations

of corrosion like anodic polarization, salt spray testing, and cathodic disbondment experiment. Studies of chemical resistance of all these coatings proved stronger strength to alkali, providing much greater protection against concrete alkaline environment. Time was conducted to crack the analysis of coated and uncoated concrete bars. In the case of uncoated bars, maximum current was achieved within 4 days, whereas for those coated with epoxy PANI primers, it took almost 50 days. Researchers conclude that repassivation triggered by PANI provided this extra protection.

Different dopants could be used for enhancing conducting polymers conductivity property and corrosion performance. Poly (methylmethacrylate-co-acrylic acid)-doped with PANI coating films have been utilized on AA3104-H19 aluminum compound through immersing the pre-treated surfaces into the polymers saturated ethyl acetate solution [45]. While these primers were non-uniform, porous and allowing electrolyte permeation, it was discovered in this research to provide stronger corrosion performance relative to a viable epoxy fabric (ICI-640C692). The sort of doping material and base coat (top coat) that is utilized has a powerful effect over corrosion protection [46].

Together with PANI, Kalendova *et al.* [47] investigated the effect of inorganic solvents such as zinc phosphate, calcium borate, and zinc powder to protect metals from corrosion. Figure 17.4 shows SEM images of PANI with different magnification.

They discovered a synergistic impact that was more effective than a simple defense mechanism in protecting metal. Loading of PANI at 2.5% w/w in water (H_2O) propagate alkydes in nano particulate shape led in enhanced corrosion productivity for metal substrates of these water-based alkyd materials [48]. PANI powder has been chemically produced and used as a pigment within a strength range of 10%–15% to

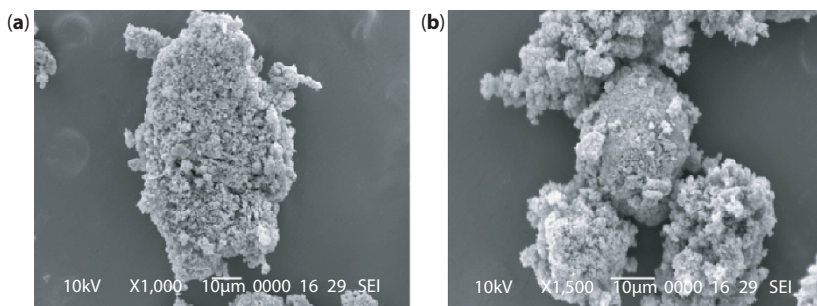


Figure 17.4 SEM images of PANI particles at different magnifications (a) 1,000 and (b) 1,500 [47].

improve the corrosion resistance of mild steel by 10–15 times in 3.5% NaCl [49]. It has been shown that duplex coating consisting of cerium alteration coating layer that act as compliance promoter and PANI utilized on aluminum component AA6063 exhibits efficient protection capability [31].

There are many difficulties with the direct application of conductive polymers coatings. Due to the insolubility and non-fusibility of polymers, their application on active metals becomes difficult. Several techniques were attempted to overcome problems of solubility, which includes chemical modifications and well-designed functional group attachment, resulting in solubility in a given medium. To increase overall conductivity, dopant anions were introduced. Several scientists have attempted to functionalize to render medium solubility in the last century. Other than solubility, surface functionalization also contributes to several characteristics being changed. Adding sulfonate groups to PANI polymer backbone changed the polymer's ion exchange characteristics, resulting in an impact of self-doping [50, 51]. Infrequently used solvents, an alkoxy and alkyl modification, were used commonly to perform polymer backbone, resulting in increased solubility. Consequently, several types of PANI and their changes can be used to protect metals and their alloys from corrosion [52].

17.4.2 Synthesis of Conducting Polymer: PPy

In the recent period, PPy has published several articles on the protection of metals from corrosion. PPy was incorporated in 1% w/w to epoxy polyamide coatings. Compared to the control sample, an increase in corrosion protection has been discovered, but greater proportions have not increased efficiency. It was noted that the effectiveness of conducting polymers relies on the application method and the circumstances under which the studies were conducted. Conducting polymers on their backbone can be synthesized with distinct anions. Dopant anion is added with conjugated polymer after oxidation of conducting polymers. When this polymer undergoes reduction, this dopant anion is released. These anions could be released as smart coatings in the coatings on demand. Dopant ions utilized in PPy synthesis have significant impact on the resulting PPy characteristics.

Kowalski *et al.* [53] investigated the bi-layered conducting polymer PPy coating on carbon steel. In this scheme, molybdophosphate and phosphate ions were doped into the inner layer, while naphthalenedisulfonate (NDS) particles were doped into the exterior coating. Molybdophosphate ions embedded into the inner layer hold passive oxide films over steel and the

exterior layer doping by NDS big organic ions restrict the disintegration and discharge of molybdophosphate ions in interior layer. All these lead to an overall enhancement in the protection against corrosion. Conducting polymers electrochemical synthesis is a commonly used method for the deposition and synthesis of conducting polymers on the appropriate substrates. The corrosion behavior of electrochemically synthesized PPy and a poly(5-amino-1-naphthol) topcoat on PPy layer was investigated by Bereket *et al.* [54] using cyclic voltammetry. It was assessed that an increase in the performance of corrosion protection was accomplished as more layers of this blend were deposited.

Several scientists have made attempts for synthesizing electropolymerized PPy apart from aluminum and steel. Herrasti *et al.* [55] investigated about the PPy over copper surface and further studied. As a result, it was found that reduced porosity and consistent surface characteristics were present in the deposited layer. This was the result of conducting polymer film's constant growth rate. These deposits of PPy, formed on copper, proved great resistance to corrosion when in a mixture of 3% sodium chloride solution. It is also proved that for excellent barrier layer features and excellent redox properties, a greater monomer level of about 0.3 M should be used. Tuken *et al.* [56] attempted to electropolymerize PPy over brass and copper surfaces. They assessed superior adhesion of these PPy films to the oxidized copper, leading in stronger protection against corrosion relative to brass. They suggested a barrier effect protection mechanism exhibited by these coatings.

Hosseini *et al.* investigated the PPy, organophilic montmorillonite (MMT), along with epoxy nanocomposites and studied about the corrosion performance over aluminum surface. Epoxy/PPy/MMT nanocomposite was discovered to exhibit superior performance in corrosion referred to epoxy resin, epoxy resin along with PPy, and epoxy resin along with MMT coating. In attempt to develop increased performance, the characteristics of distinct materials can be mixed together [57]. In another researcher, in the existence of dihydroxybenzene, Tallman *et al.* [58] studied about the synthesis of nanocomposite through pyrrole polymerization over alumina nanoparticles. For coating, they used this material as filler in a ratio of less than 2%. Dihydroxybenzene was discovered to improve the adherence of coating to the surface of the aluminium. The research considerably shows the modifications caused by electrochemical impedance spectroscopy (EIS) in the shape of geometry and also volume proportion of voids occurred in the coating. The voids provide a direct effect on corrosive solution aging and penetration into the layer.

17.4.3 Synthesis of Conducting Polymer: PTh

There were few articles published on PTh to protect metal substrates from corrosion. A range of replaced PTh polymers can be synthesized. Compared to other conductive polymer derivatives, some of PTh derivatives perform very well. This eventually depends on the environment nature that is exposed to these conducting polymers. The combination of these two led to improved PTh and also its derivative could be produced by other conductive polymer substrates such as PPy with the proper application of voltage. The combination of these two led to improved performance in corrosion.

Kousik *et al.* [59] used acetonitrile as a medium to produce PTh coatings on mild steel (MS) layer. It was determined by AC impedance analyze and resulted that PTh film coated in MS was shielded by a process of triggered passivation by PTh redox operation. Studies of water absorption and the delamination region also verified electropolymerized PTh protective effect on mild steel layer. Ocampo *et al.* contrasted many marine anticorrosive paints with PTh derivative being added. It was discovered that adding a low poly (3-decylthiophene-2,5-diyl) content (0.2% w/w) improved the productivity of corrosion resistance of epoxy-based plastics.

The role of distinct layer treatment over the substrate was explored by Rammelt *et al.* [60]. On the surface of MS, homogenous and well adherence polymethylthiophene layer were developed subsequently treatment with 2(3-thienyl) ethylphosphono acids. The polymethylthiophene layer films were ultrathin and extremely organized (thickness was about 1 nm). By using ultrathin films, they showed stronger protection with energy costs. These films have been discovered to efficiently distinguish oxygen decrease and iron dissolution electrochemical processes in the surface area.

17.5 Performance Improvement and Bulk Modifications of Conducting Polymers

The difficulty of insolubility about conducting polymers in sedimentary condition, the complexity allied with preparation, and low or medium anti-corrosive efficiency insisted some structural modifications and also synthesis characters. The several methods that improve the synergistic effect include doping, copolymerization, layering, and its combinations.

17.5.1 Doping

The process of doping which enhances the corrosion of conductive polymers arises from the intention of exchange between the anions like sulphates, chlorides, nitrates, etc., with polymers in the presence of electrolytic solution. Also, it is assumed that the failure of coatings arises due to the diffusion of corrosive species over the coating later.

17.5.2 Layering

Layering implies the formation of various films of polymer over the metal surface. The option of having a multilayer [54], trilayer [61], and bilayer [62] coatings of polymers over metals has been carried out by many researchers. The advantage of using this method has also been discussed by industrial ion interchange resins [63] and ion membranes [64]. In the layering method, the interior layer acts as anodic protecting where the exterior layer acts as barrier. Bilayers of conducting polymer polypyrrole with poly(5-amino-1-naphthol) [54], polyphenol [65], organosilanes [66], and cataphoretic [67]; polyaniline/polybithiophene [68], polyaniline/poly(N-methylaniline) [69], and polyrhodanine/isobutyltriethoxysilane [54] were discussed that they exhibit superior adhesion and effect of anti-corrosion over metal substrates when compared with the mono-layers.

17.5.3 Copolymerization

Based on the literature studies, it is evidenced that copolymerization elevates the properties of polymers [70]. Copolymerization is generally defined as a combination of two or more monomers when combined with each other for producing a new compound with different properties. It is generally an end product that connects the benefits of the monomers excluding the disadvantages of it. This copolymerization may overcome the drawbacks of poor solubility, porosity, and bonding property of conductive polymers and enhance the corrosion characteristics [71]. Srikanth *et al.* [72] identified that on copolymerizing aniline with N-methyl aniline, the resulted copolymer that protected the surface of carbon steel in hydrochloric acid medium with 81.2% as compared with 18.8% for polyaniline and similarly 56.3% for poly(N-methyl aniline). Another important parameter regarding copolymerization is about the modification of copolymerization characteristics as per the requirement of altering the ratio of both the monomers that is going to be adopted [73].

17.6 Conducting Copolymer Composites and Nanocomposites

Many investigations have indicated the capacity of utilizing copolymers as anticorrosive coatings. Generally, composites are the combinations of diverse materials with different functional properties for corrosion behavior of metals and its alloys. Various metals, metal oxide particles graphene, and carbon-based nanotubes particles can be integrated with PANI matrix for production of PANI based nanocomposite materials [74]. To evidence the improvement in protection capacity of PANI composites over a MS substrate, coating over PANI with zinc and its nanoparticles were made of iron by adopting solvent mixing technique [75]. The existence of Zn nanoparticles in PANI showed improved anticorrosion and conductive property when compared with coating of micro sized particles of Zn on PANI matrix. Also, the impact of filler materials has improved the properties of the base materials.

Another study indicates that on implementing chemical oxidative polymerization for production of PANI-Zn nanocomposites. The prepared nanocomposite was then adopted on iron substrate using solution casting method. It is also evidenced that 5% w/w loading maximum conductivity was achieved. Also, it was clear that the amount of zinc decides the conductivity property of PANI-Zn nanocomposite. The pores in the CPs are filled by corrosion products of Zn which results as barrier protecting medium along with electrochemical property of CPs [76].

PANI composites with carbon-based nanotubes were utilized as pigments on low carbon steel for superior anti-corrosion property [77]. It is also evidenced that this PANI-CNT-based paints drastically reduce corrosion property of steel in 3.5% sodium chloride solution evidenced through Tael polarization and Electrochemical Impedance Spectroscopy studies. Also, the PPy and ZnO nanocomposite coatings have depicted enhanced corrosion resistance property when compared with PPy coating. This ZnO utilized was in the form of nanorods which was clearly evidenced in studying morphology which generally contributed to the corrosion properties of composites [78].

In some other investigation, PANI clay nanocomposite were fabricated using a chemical oxidative polymerization method [79]. The same was then added with zinc-rich ethyl silicate resin. Then, Electrochemical Impedance Spectroscopy measurements were done in 3.5% sodium chloride solution was noted for evaluation of corrosion. The protection barrier and also passivation of metal substrate owing to the existence of nanocomposite

indicated improved corrosion resistance by coating PANI-clay nanocomposite when compared with pristine coat.

The conductive polymer that contains composite coating is newer materials that were developed for resolving the processability characteristics related to conducting polymer. PPy with aluminium flake composite have identified for protecting aluminium alloy from corrosion [80, 81]. This was identified that PPy wire forged in the surface of Al substrate resulting in formation of PPy/Al composite that provides corrosion protection to the substrate. Also, Phosphate and nitrate doped composite were applied on surface of the material which protected the substrate from corrosion. Also, redox property of PPy in combination with barrier properties of MIOX indicated superior corrosion protection [82].

17.7 Summary of Conducting Polymers-Based Protective Coatings

Different approaches that are adopted for development of conducting for protective coatings were summarized in Figure 17.5. This sorting helps for choosing conducting polymer formulation which depends on many factors which include period of protection requirement, structure, composition, and pH value of the corrosive environment. The latest studies reveal about the corrosive protection conducting polymer-based coatings mainly focuses on organic and inorganic composite coatings. It was also found that these protective coating offers long term superior protection to metal

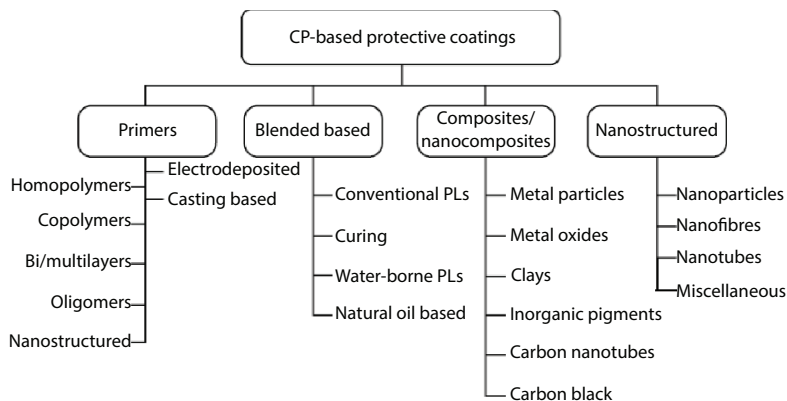


Figure 17.5 Different forms of conductive polymer-based protective coatings.

surface and also self-healing property by organic coating in concurrence with the reduced effect evidenced for inorganic pigments.

17.8 Conclusions

Various conductive polymer coatings have been utilized for protecting the corrosive medium. Different coating methods, *viz.*, zinc rich coatings, inhibitive coatings, conducting polymer-based coatings, chemical oxidative polymerization, and electrochemical polymerization methods that were used for corrosion resistance protection have been extensively discussed. Also, methods of synthesizing conducting polymers for corrosion protection were demonstrated. The performance improvement studies and also bulk modifications of the polymers which improve the effect that includes doping, copolymerization, and layering for corrosion improvement have been studied. Also, various forms of conducting polymers that were utilized for protection of metals and its alloys from corrosion have been studied. These conducting polymers are used for multilayer coating, pigments, and composites. Also, the corrosion protecting dopants can also be included over the backbone of conducting polymer for protection in particular conditions. The morphological properties influence the anti-corrosion properties of such conducting polymers. Improved protective coatings have been developed for better performances of the substrate have been investigated. Enormous studies regarding the protective coating of conductive polymer base materials have been done for enhancement of anticorrosion behavioral properties.

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Polymer Coating for Industrial Applications

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Abstract

This chapter presents extensive research studies reported by worldwide scientists and specialists in the area of polymer coatings for industrial applications. The authors discuss new and emerging industrial applications, including micro systems, oil and gas industries, electronics, biomedical, pipeline, automotive industries, micro bit storage systems, corrosion protective, and anti-bacterial coating. The authors address the potential to improve and increase the marketability of polymer coating applications in future research in these fields. To date, extensive research has been initiated in order to identify new biodegradable polymer materials which could fulfill all the features needed for the desired quality of the eco-friendly polymeric coating materials.

Keywords: Polymer coating, bio-medical, corrosion resistance, anti-bacterial coating, oil and gas

18.1 Introduction

The word “polymer” is often used to define the multiple repetitions of macro molecules of one or even more units united to offer a set of characteristics.

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They are categorized into natural and synthetic based on their origin. Cellulose, dextran, starch, Arabic latex, chitosan, etc., are classed as natural polymers [1]. The synthetic polymers include three distinct subdivisions, namely, thermoplastics, thermosets, and elastomers. Polymers are employed in broad range of applications, including automotive sector, furniture, toys, coatings, boat hulls, glues, etc. They have attractive characteristics that depict them as important applicants for interfacial modifications against corrosion of metals. This comprises accessibility, environmentally friendly, cost-effective, reliability, and numerous adsorption centers. Under the International Guideline, it is prohibited to use inorganic compounds such as hexavalent chromium and the defined three key criteria are (a) non-bio accumulative, (b) biodegradable, and (c) no or very low level of environmental toxicity for approval of inhibitors. Most of those criteria are met by polymers in general, which naturally occur and extensive research attention has been directed [2].

The polymer films have numerous applications, such as protective coatings, sculptures, liquid and gas isolation barriers, storage and processing materials, semi-conductors, micro fluidic systems, optical instruments, fluorescent sensors and drug delivery and encapsulation, acoustic devices, and biomedical applications. Owing to their phenomenal characteristics like electrical, chemical, and optical with strong chemical and mechanical strength, multilayered, and hybrid multi-layer have attracted a lot of research [1]. We thought the time is absolutely correct for a detailed analysis of different applications of polymers coating. This chapter will provide necessary information for the scientists working in this field, student's community, and industry.

18.2 Polymer Coating in Oil and Gas Industry

The petroleum industry has extensively employed several polymers to sustain, treat, and improve the process of drilling and extraction in oil and gas well. Polymers minimize heavy well accumulation, preserve fluid viscosity, dense air, reduce corrosion, and maintenance downtimes, but also allow for surface cleaning of machinery and wells. The coating of a proppant during hydraulic fracturing HF operations is one of the most common forms of polymer usage in oil and gas industry. Proppants are small areas which have to possess sufficient strength to effectively deal with high locking stresses. Polymers have been introduced in recent years as a coating for proppants and promise increased performance, taking into account both the significance of strength and flexibility. The coating of the proppant

with a thin polymer layer leads to increased conductivity of fracturation, decreases fines and scaling considerably, and improves the quality of HF treatment as a result. Polymers (e.g., resin) can be used to enhance the performance of proppant and to keep together many of its coating grains. As shown in Figure 18.1, sand is compressed by increased closed pressure and fines are released when it crushes.

The result of this failure is fine development and restricted conductivity of fracture. Proposed backflow, fine generation, supportive scaling, and low conductivity to fracture constitute the most common problems caused by incorrect choice of proppant. Crush occurs when the stress of fracture closure reaches the maximum strength of proppant. This leads to fines that can transfer, relocate, and block a proppant pack, which diminishes the output of wells. Due to lower width, loss of fracture conductivity can be caused. It can lead to additional compounded flow back, fine formation, and scaling. By employing polymer coating, many of the fines may be encapsulated by the polymer, so it can lead to the treatment of HF successfully [3].

Polymeric products provide better resistance to temperature and corrosion; low friction, low wear resistance; low noise emissions; and low production cost [4–6]. Hence, it is appropriate material for the tribological applications. Severe corrosion could be effectively reduced in petroleum and gasoline industry [7–9], if polymer coatings were applied on the surface of steel. In broad aspect, their wear resistance is a problem because polymers, especially for the thin film covers, are soft materials. Aromatic polyester oligomers discovered in the middle of 1990s [10], which is produced as a result of curing cross-linked oligomers. The transition temperatures are diversified based on type of oligomers. In past tribological investigations on tilting pad layers and compressor settings [11, 12], ATSP polymer layers were shown to be extremely low wear levels, high temperature working, and excellent abrasive wear resistance [13, 14].

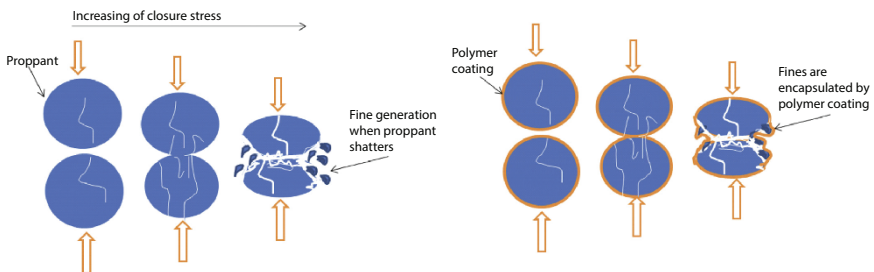


Figure 18.1 Polymer coating on proppant [3].

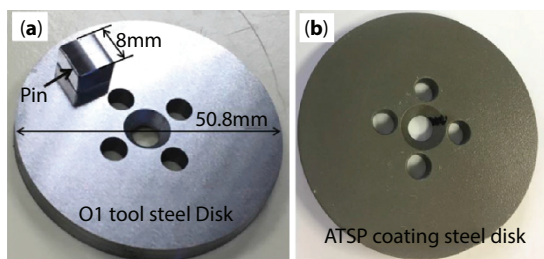


Figure 18.2 Photographs of samples, (a) O1 tool steel disk and pin, (b) ATSP coating on O1 tool steel substrate [15].

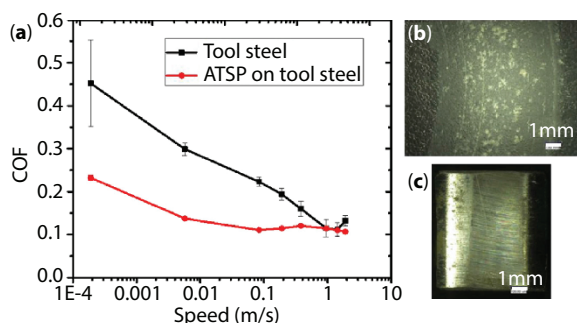


Figure 18.3 Experimental results of Stribeck curve analysis, (a) COF vs. sliding speed. Error bars designate one standard deviation, which in some cases are too small to show. Optical microscopy images of (b) ATSP coating, and (c) pin, after the experiments [15].

A research study on ATSP has been developed to mitigate COF as a cost-effective coating in oil and gasoline drilling operations. The test samples included in this research study were thin layer ATSP coated pure tool steel and curved pins as shown in Figure 18.2. In ASTM standard D2714 and standard for block-on-ring evaluation-D3704, the O1 tool steel is typically used. The powder sample of ATSP with the wt% 98.6 and PTFE with 1.4 was applied to 35 μm thick ATSP layer using an electrical spray deposition process, followed by a 30-minute cure at 270°C in warm air [15]. COF of ATSP coating predominantly depends on mechanical characteristics of coated layer and hence possesses a constant COF as depicted in Figure 18.3 [15].

18.3 Polymeric Coatings for Tribo-Technical Applications

Polymer coatings are now widely spread over the industrial process by refilling them with strengthening or usable inclusions. Forced, thermal,

and other types of loading are applied to coatings deliberately designed for tribo-technical implementation. Coatings made from composite materials on a polymeric matrix are employed extensively because in combination with easy and quick sliding, they can offer better corrosion resistance and nominal friction. The phase of loading at the interface matrix inclusion reflects an individual deformation and fracture structural issues [16]. Coating wear is associated with material fractures in stress areas, but the surface is important because the load is applied locally on it [17]. Such concentration may be controlled by the following criteria: (1) the load is non-uniformly applied, (2) the substratum's surface is non-flat or specially shaped, (3) loaded polymer structure, and reinforcing inclusions serve as stress concentrators [18].

In experimental studies of a coating rendered from structurally and functionally modified UHMWPE filled with micro- and nano-fillers, the impact of elements at different level on the mechanical, physical, and tribological characteristics of UHMWPE was shown [19]. The polymeric matrix properties are influenced by the existence of amorphous and crystalline phases and should be taken into consideration when analyzing SSS variables of the UHMWPE-based polymer composite. This factor permits the computation on the fourth level of structure–Mesoscale III, as shown in Figure 18.4 [18].

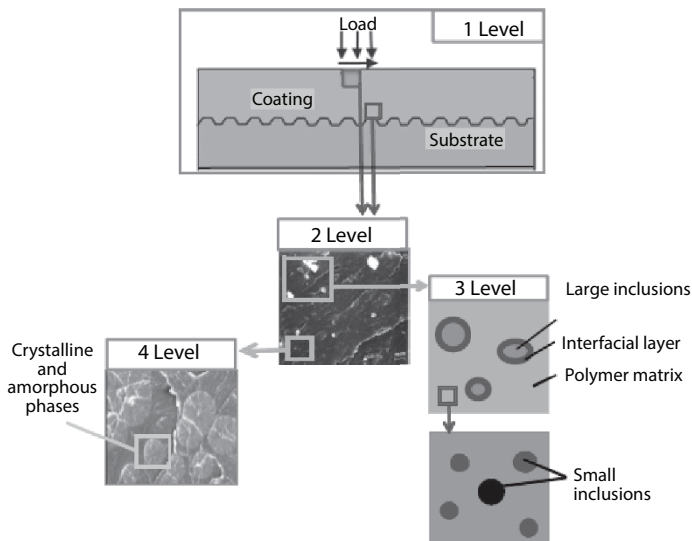


Figure 18.4 UHMWPE-based polymer composite [18].

18.4 Polymer Coating for Drug Delivery

Systematic and regulated drug delivery systems have many advances over traditional drug delivery methods, such as lower soluble drug delivery, very low dose toxicity, controlled drug release kinetics, which extend the reach of treatment [20, 21]. Because of these benefits, various medicines for the controlled release have been developed such as surface-deposited coatings for hydrogen [22–24], nanoporous, polymeric micelles, nanoparticles, water-soluble polymers [25, 26], liposomes, poly-(L-histidine) pH-reliable nano particles, etc. Over recent times, antimicrobial coatings have been developed from silver nano particle-based, amine-based materials. Plasma polymerized n-butyl methacrylate (PPBMA) coatings and n-heptylamine films are employed as a barrier layer for controlled and regulated drug delivery [27, 28].

PCL has been broadly explored as a core polymer membrane in 3D tissue engineering scaffolds and controlled with regulated drug delivery systems. Functional surfaces provide the possibility of increasing biological activity, but the lack of functional groups in the PCL-homo polymer interfaces bounds their application. Figure 18.5 shows the schematic of layer

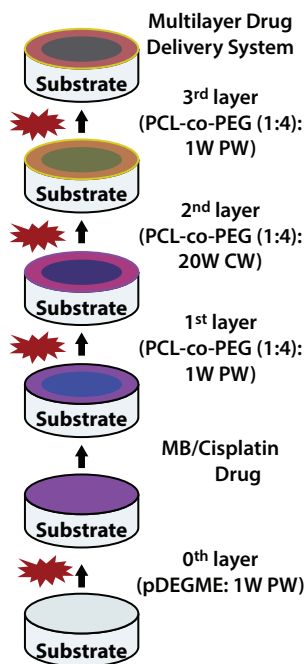


Figure 18.5 Multilayer coating for drug delivery [29].

deposition. Various pretreatments have been researched in order to introduce functional groups on PCLs like aliphatic polymer surfaces. Due to hydrophilicity, anti-toxicity, and lack of antigenicity and immunogenicity, selected PEG can be copolymerized with PCL [28, 29].

18.5 Polymer Coating for Corrosion Protection

Corrosion, with annual worldwide cost of USD \$2.5 trillion, equivalent to 3.4% of the world's GDP, is a global challenge. Loss of corrosion is divided into direct and indirect. The costs of repairing corroded or broken equipment and machinery, painting, and refinishing rust prevention structures, the cost of other precautionary measures, the additional cost of utilizing corrosion-resistant materials and alloys, and the expenses of dehumidifying metal storage rooms are taken in consideration of direct losses [30]. Metallic surfaces are a very important concern in protecting them from corrosion. The development of surface treatment method, which would provide proper durability of corrosion protection of metals, is important depends entirely on the metal and surrounding in which it is exposed. In the past decades, a protective coating has been an important consideration for the corrosion protection of metals [31].

Conductive polymers (CPs) are effective in the area of corrosion protection because of their environmental reliability and can easily be developed by chemical or electrochemical approaches. The benefit of alternative methods is that the utilization of organic solvents minimizes the need for contaminants-free polymers [32]. The performance of the CP coating is influenced by a set of experimental factors, such as electro-synthesis, pH and composition of polymerization, that are implicated throughout electro-polymerization [33].

Research effort has been performed to electro-polymerize a pyrrole and aniline mixture known as composite, utilizing a cyclic voltammetry technique, on a pre-treated aluminum surface of Al2024-T3. The anti-corrosive properties of the developed coating were studied with respect to sweep frequency and concentration. Characterization of the coating carried out via cyclic (CV) voltammetry and microscopy. A CV is an appropriate method for the electrochemical properties characterization of CPs, representing the systasis of polymer coating. The bibliography includes limited work on the deposition of specific polymers on aluminum substrates [33–36]. Some researchers have the deposition by potentiostatic or through CV of a combination of pyrrole and aniline, while others try to place sequential layers of the many polymers that create a sandwich-like structure [36].

18.6 Polymer Coating for Antibacterial Activity

The utilization of polymers containing the functionality of antimicrobials to improve the effectiveness of certain known antimicrobial agents, mitigate ecological problems with traditional agents, and increase lifespan of anti-microbial agents was extensively explored. The blend of antimicrobial polymers and nanosilver symbiotically improves the effect of bactericides, while polymers typically have a significantly weaker bactericidal efficacy than nanosilver. In order to increase antibacterial property, the polymers could alleviate and dissolve nanosilver [37, 38].

The probability of inhibiting accumulation of nanosilver and creating a uniform top surface coating on different materials is pronounced by polymeric materials with great adaptability and versatility. Such materials can also monitor silver iodine concentrations to mitigate cytotoxicity and persistent antibacterial impact. These can be designed more specifically to prevent adhesion to bacteria and to boost bactericidal properties. It is thus advantageous, for the antibacterial applications, to produce nanomaterial (nano silver) embedded in polymer matrix to develop multifunctional compounds. The composites of polymer/nanosilver with various forms, particularly the influence of shape of fiber had been thoroughly explored. Nanosilver can, on the other hand, play an important part in the medium-term antibacterial impact of developed polymer/nanosilver coatings with a stronger bactericidal property than polymers [39, 40], whereas bactericidal polymers can dominate in long or stable antibacterial coatings following depletion of polymers in silver ions. Figure 18.6 shows the procedure for deposition of amine groups embed with silver nano particles on substrates for anti bacterial activity [41].

The main categories of bactericidal polymers are the quaternary ammonium-based polymer compounds (QAC) [42, 43]. A polymer based on a QAC usually consists of three parts: the polar alkyl chain, cationic compounds, and spacers. The spacers shall ensure that antibacterial effects are transferred by cationic groups. The combination of the QAC and hydrophobic alkyl chain gives a potential antibacterial effects hole poking mechanism. The alkyl chain can have a significant impact on antibacterial properties through a high level of lipophilicity, which can cause effective structure damage and integrity of the cell membranes. A polymer-silver nanoparticle embedded coating on polyethylene terephthalate flat surfaces has been synthesized from N-hexyl-N-(4-vinylbenzyl)-4,4-bipyridinium di nitrate. The composite coatings are pretty highly antibacterial to *E. coli*

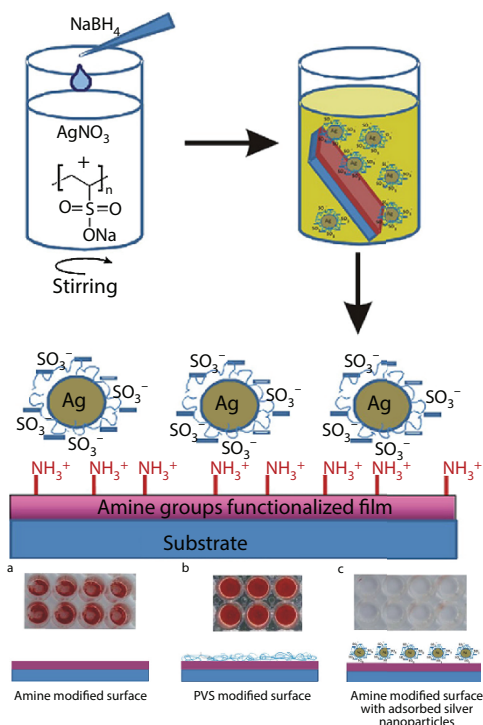


Figure 18.6 PVS modified amine coated substrates [45].

and stay stabilized after sustained immersion and ageing in the weathering channel in the phosphate buffer solution [44].

Chitosan is a functional and natural polymer extracted through deacetylation of chitin which exhibits enhanced anti-bacterial properties and biocompatibility. A number of potential mechanisms for interpreting its antibacterial activity have been suggested. Composite coatings for antibacterial applications of chitosan/heparin/nanosilver had prepared. *E. coli* has a good bactericidal effect in the composite coatings without substantial mammalian cell cytotoxicity. The effective antibacterial property may also last 1 month. There have been studies of other bactericidal polymers, including poly hexamethylene bi guanides, polymers incorporating furanones, polymers bound to antibiotics, and antibacterial peptides. While these polymers have significant potential for combination with nanosilver to produce composite polymer/nanosilver coatings, very little is still used. They should, therefore, bring enormous possibilities for future research [44, 45].

18.7 Polymer Coating for Micro Bit Storage

Currently, the versatility of associated processes and remarkable materials attracted attention from the work of vinylidene fluoride (VDF)-based ferroelectric polymers. As far as processes are concerned, ferroelectric film can be deposited through various means, such as physical, chemical vapor deposition, Langmuir-Blodgett, and solution methods. Their physical characteristics would often be modified by altering the molecular structures synthetically with distinct moieties. Mechanical adaptability and transparent optical visibility enable ferroelectric polymers to be used in transparent film applications [46].

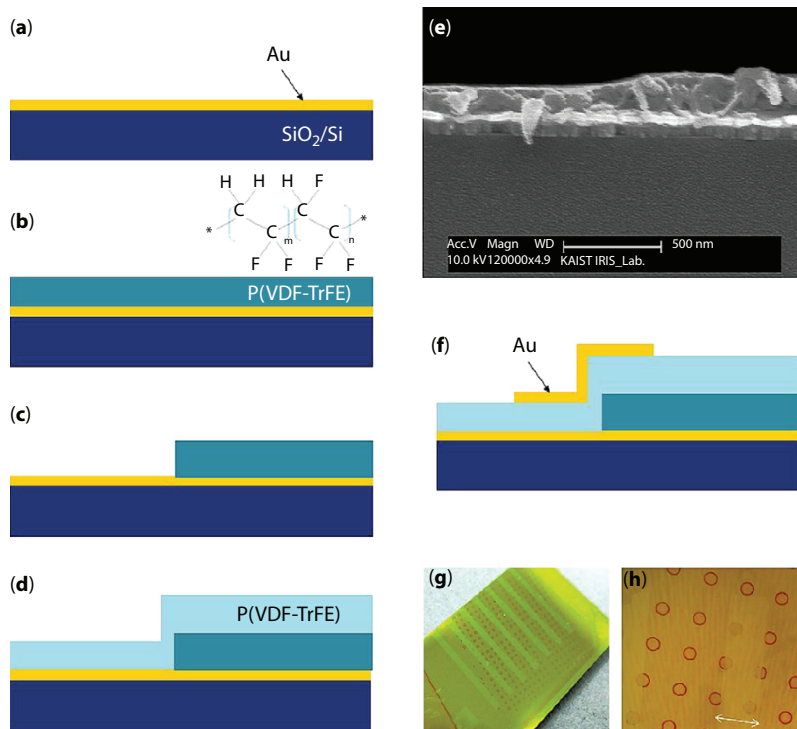


Figure 18.7 Process flow chart: (a) Au-deposited SiO₂/Si substrate; (b) ferroelectric polymer, P(VDF-TrFE), spin-coating; the chemical structure of P(VDF-TrFE) is depicted and the ratio of m and n is 0.75:0.25. (c) patterning of the ferroelectric polymer film; (d) conformal double-coating of the ferroelectric polymer film; (e) cross-sectional SEM image of sample after process (d); (f) deposition of the Au top electrode; (g) photographic image of the final sample; (h) microscopic image of the final sample. The white scale bar represents a distance of 500 μm and the area of the top electrode (circle) is 2.54×10^{-4} cm² [46].

The subsequent environmental inertness enables for a non-volatile storage medium. Applications such as multi-bit storage media are investigated using these characteristics of ferroelectric polymers. One research study found that a condenser consisting of a two varying thicknesses had been used to manipulate the morphology of ferroelectric polymer film by simple indentation with a rigid mould as depicted in Figure 18.7. This sort of condenser can be used as a multi-bit memory device if a surface electrode surrounds two areas simultaneously with varying thicknesses [46].

18.8 Polymer Coating for Micro Batteries

Three-dimensional micro batteries (3DMBs) explore new prospects for small energy storage solutions that can react to combined heavy power and energy density requirements. Three-dimensional micro batteries are a key element of this approach. In addition, it is necessary to identify appropriate electrolyte mediums that ion conduction and electron-isolation, conformal, or pinhole-free but nevertheless mechanically or electrochemically sustainable in contrast to the implementation of a latest 3D nano-architectural electrodes. Solid polymer electrolytes (SPEs) offer increasing protection and versatility in a range of architectures and electrode properties compared to standard liquid electrolytes.

An ionically conductive polymer surface subsequently deposited on these structures will represent an important step forward to finalize 3DMB. The oligomer poly(ether amine) (glyceryl poly(oxypropylene); PEA), that has surfactant characteristics, is to be mixed in a cross-linked polypropylene glycol (PPGDA) network to develop uniform and smooth electrolyte coatings on complex electrode surfaces, for practical utilization within 3DMBs. The work presented concentrates on the synthesis and evaluation of a unique solid polymer element that consists of statistically-replaced PEAs at one of ends of three oligomer chain and one methacrylic group at the average. This change incorporates a bi-functionality of a PEA monomer, which becomes polymerizable as well as a surfactant, as the substitution of a PEA/PPGDA electrolyte system [47].

18.9 Polymer Coating for Biomedical Applications

Anti-corrosion strength of biomaterials has been enhanced by employing coatings in many respects. There were anodized coatings but they have been found to decrease corrosion and prevent magnesium degradation. Other protecting materials have also been examined, like organic polymers and hydroxyapatite,

which minimize corrosion while still allowing to some degradation. Moreover, some of these coatings are avoided from employing to implant materials due to lack of mechanical properties (especially in adherence and cracking).

No optimal coating that permits degradation at a suitable rate thus sustaining mechanical integrity has yet been established, regarding current research. Two-layer bio ceramic-polymer architecture is known to increase the adhesive capacity of the polymeric film, if the bio ceramic coating is well attached to the substratum and has a large surface area. The goal of a research study was to improve mechanical integrity and to control corrosion levels by applying polymer-bio ceramic composite films to magnesium. The bioceramic layer was chosen for bio active hydroxyapatite and could stimulate bone development. Polylactic acid (PAL) has been selected as the biodegradable polymer coating and is also provided with the additional benefit of FDA approval for application of implants [48].

Alternative layers of photozyme-graft copolymer, Chitosan-g-fluorescein and photocymestatic polymer, poly (sodium styrene-co-vinyl naphthalene-Co-3-dimethyl (methacryloyethyl) ammonium propane sodium sulfonate) -ZI, the nanoscale, multi-layered photo active films have been coated with genipin-crosslinked gelatin substrate by means of the LbL technique

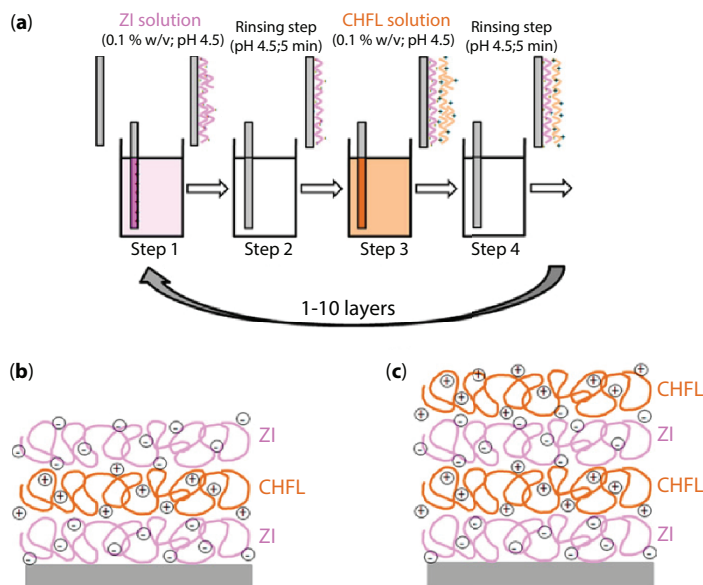


Figure 18.8 Scheme of (a) the method for the modification of G_GP substrate via LbL method, (b) an anti-microbial multilayer promoted by ZI photozyme and (c) anosteointegration improvement multilayer induced by CHFL photozyme [49].

as depicted in Figure 18.8. Nano coating was distinguished by morphological and physicochemical studies. Owing the photosensitizing characteristics of distinct sorts of photozymes, nanostructured materials produced can have significant applications as multifunctional coating for bone repair materials. In order to imitate the cycle of natural bio mineralization, the development of bone-like carbonates apatite layer on the engineered scaffolds includes bio-mimetic scaffolding for the one tissue engineering [49].

Certain biological liquids that surround hip joint do not damp the surface enough, resulting in increased friction and eventually release wear debris. It is probably due to HMWPE in aqueous biologically based body fluids being hydrophobic. Recent work has been investigated in order to develop a wettable layer, minimizing wear particles due to abrasion and the graft of hydrophilic, biocompatible polymers to the surface of HMWPE. The grafted polymers must therefore be deposited on the top surface of hip implant, not only for bio-compatibility, but robust enough for the anticipated friction movement during usage. For use in multiple applications of medical devices, polymer coatings can be developed to have unique chemical, mechanistic, and physical characteristics [50].

18.10 Polymer Coating for Pipe Line Applications

In recent times, polymeric materials were extensively used in numerous industrial applications, particularly in pipe coating. Such coatings are employed mostly for resistance to corrosion, but also as a mechanical damage protection. For these applications, several polymeric materials are used, including polypropylene, ethylene butyl acrylate, fusion bonded epoxy, and high density polyethylene. Currently, in the pipe industry, polyethylene coating has become progressively predominant, and Figure 18.9 portrays the pipe line polymer coating. Furthermore, it constitutes a reliable, elevated-performance, and economical layer of protection against metal [51].



Figure 18.9 Polymer coating for pipe lines [51].

18.11 Conclusions

The chapter provides an overview of polymer coating and its industrial applications. Polymeric products provide better resistance to temperature and corrosion; low friction, low wear resistance; low noise emissions; and low production cost. Hence, it is appropriate material for the many industrial applications. The numerous applications of polymer coating such as protective coatings, sculptures, liquid and gas isolation barriers, storage and processing materials, semi-conductors, micro fluidic systems, optical instruments, fluorescent sensors and drug delivery and encapsulation, acoustic devices, and biomedical applications have been discussed elaborately in this chapter.

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Formulations for Polymer Coatings

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Abstract

Over a previous couple of decades, polymers are widely used as pharmaceutical excipients in many novel and conventional drug delivery systems from being merely used as gelatin shells to contribute massive formulation benefits such as controlled/sustaining the drug release and also targeting of drugs to the specific site, consequently hold a considerable clinical promise. Currently, numerous dosage forms are provided with diverse coating techniques, which may give out a variety of functions. Based on functionality, several polymer coatings are available commercially to offer incessant formulating choices. In this chapter, recent advancements in the usage of polymers for coating of different dosage forms such as tablets, capsules, implants, nanoparticles, and liposomes, etc., are discussed. Mechanisms of polymeric film formation and applications of polymer coatings in the different areas of biomedicine are clearly explained. Application of different polymers in various coating functions is extensively reported.

Keywords: Enteric coating, colon targeting, natural polymers, biomedicine, taste masking, moisture protection

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19.1 Introduction

The coating is a method by which an outer dry layer of coating material (containing polymers and other excipients) is applied to the dosage form surface (core) to confer specific benefits. Coating of pharmaceutical dosage forms is one of the regular unit operations in the industry. The basic concept of sugar-coating technology was borrowed from the candy industry in the mid-1800s to coat the tablets contain bitter drugs [1]. In recent days, film coating process predominantly replaced by the sugar-coating process by making use of polymers, which will produce a very thin film on applying to the substrates. By selecting the appropriate polymer-drug release profile can be tailored. Product differentiation, chemical protection, and separation of incompatible drugs are some of the other advantages. The coating process can also increase the packaging speed by reducing the dust generation and friability [2]. The applications of coating mechanism not only constrained to pharmaceutical filed but also to biomedicine and other engineering areas. This chapter summarizes application of different polymers for coating of different dosage forms like tablets, capsules, liposomes, pellets, etc. Application of coating process in different areas of biomedicine is clearly explained.

19.2 Film Coating

Film coating process involves deposition of very thin polymeric film (approximately 25 to 100 μm in thickness) on to the different solid surface substrates such as tablets, granules, or capsules to i) alter the drug release, ii) protect the drug from various environmental/physiological factors, iii) to enhance the physical and chemical properties of the substrate, iv) mask the unpleasant taste and odor, and also v) to avoid the interaction of various incompatible ingredients. Functional coating such as modified release, osmotic pressure-controlled drug delivery system, and enteric coatings can be done for advanced drug delivery systems. Film coating process ensures for batch to batch uniformity as well as good reproducibility [3]. Coating formulation majorly contains polymers, plasticizer, anti adherents, surfactants, and colorants.

19.2.1 Polymers for Film Coating

The film-forming polymer can be classified into two major classes depending on the solubility, aqueous soluble and insoluble polymers

(pH-dependent soluble polymers). Majority of aqueous soluble polymers are cellulosic polymers such as MC (Methylcellulose), HPC (hydroxypropyl cellulose), HPMC (Hydroxypropyl methyl cellulose), CMC sodium (carboxymethyl cellulose sodium), polyethylene glycols, and polyvinyl pyrrolidone (povidone) [4]. The water-insoluble or pH-dependent soluble polymer is widely used for delay release (enteric coating) or some special controlled systems. Some of the common enteric polymers are methacrylic acid copolymers (Eudragit® E, Eudragit® S Eudragit® L), phthalates (cellulose acetate phthalate-CAP and hydroxypropyl methylcellulose phthalate-HPMCP), polyvinyl acetate phthalate (PVAP), in addition to EC (ethylcellulose), PVA (Polyvinyl acetate) Eudragit® RL and RS grades [4].

19.2.2 Plasticizer

During the coating process, on drying films prepared from pure polymers as often as possible are fragile. To deal with this insufficiency or to make the film more pliable, the polymer can be modified chemically by making use of some excipients such as plasticizers [4]. Plasticizer allows/helps the polymer molecule to move easily and also have the capability to weaken the intermolecular attractions [5]. This will result in enhancing the flexibility of the polymer, improving flowability, increasing the toughness, reducing brittleness, and improving the tear resistance of the film. Plasticizers can broadly classify into two major categories: internal and external plasticizers, based on inclusion or addition of plasticizer in the coating process. Internal plasticizers can modify the physical properties of basic polymer by altering the degree and type of substitution or polymer chain length of or both. The external plasticizer acts by enhancing the flexibility of the film by modifying the polymer-polymer interactions and by relieving molecular rigidity [4].

19.2.3 Polymer-Plasticizer Compatibility

The plasticizer must be compatible with the polymer, so as to form continuous film and to make the formulation successful. The foremost difficulties while formulating the coating solution are i) selection of proper plasticizer, ii) assessment of the interaction of polymer with plasticizer, and iii) perception of mechanism, how the plasticizer is improving the flexibility of film. Methods to predict the compatibility between plasticizers and polymers are on basis of i) solubility parameter calculation using molecular dynamics, ii) molecule charge density by using COSMO, iii) experimental DSC analysis, and iv) mesoscale simulation using endeavors.

The impact of plasticizer on polymer properties have been studied by many researchers, a few of them are given below. Results from DPD simulations confirmed the compatibility between polyethylene glycol (PEG) and PVP, as PEG mix well with the PVP. DSC results showed that there is a superior interaction between HPMC and PEG than between MCC and PEG, because of higher degree of miscibility and attraction of HPMC with PEG molecules in contrast to MCC [6]. The impact of the plasticizer (PEG) on mechanical strength and thermal behavior of coating films (HPMC) was studied by Labouffie *et al.* [7] Jarray *et al.* [8] additionally examined the affinity of the base polymers with the coating in both dry and aqueous systems. Ould-Chikh [9] found that addition of the plasticizer (PVA) to the aqueous polymeric suspension noticeably minimizes the cracking or segmentation of coating films after drying.

19.2.4 Mechanism of Film Formation

Depending on the solubility of film coating polymers, film coating applications are mostly solutions or dispersions [10]. Film formation mechanism from dispersions is more complex in contrast to solutions [11]. On applying the polymer solution, a bond is formed between the coating polymer molecules because of the cohesion forces between them; whereas in case of dispersion, film will be formed as a result of coalescing between the polymeric particles.

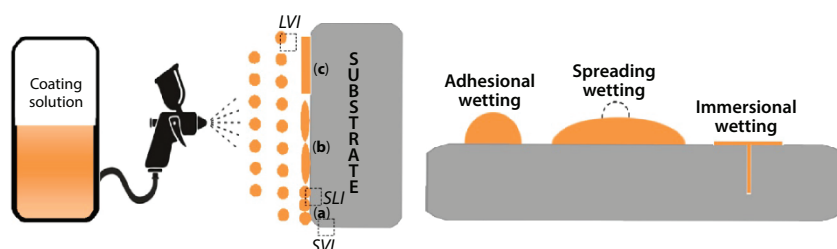
Generally, film coating is applied by spray atomization process. On spraying, the formed droplets spread on the substrate, and with further drying, the solvent evaporates, and polymer chain interpenetrates and forms the film. The degree of spreadability of droplets relays on surface tension. Several surface tensions are involved in the coating process like a) liquid-vapor interfaces (LVI), b) solid-liquid interfaces (SLI), and c) solid-vapor interfaces (SVI). Spreading of the droplets can be described by replacement of SLI or SVI. The wetting mechanism or replacement of interfaces can be mainly of three types such as adhesion, spreading, and immersion wetting. Replacement or formation of interfaces is depends upon the type of wetting mechanism (Table 19.1). Figure 19.1 describes the surface tensions relevant and types of wetting mechanisms in coating process.

The coating process can be considered as a complex phenomenon, owing to the number of processing variables and their interactions, variables related to the coating formulation, and substrate properties.

Table 19.1 Replacement or formation of interfaces with the type of wetting mechanism.

S. no	Type of wetting mechanism	Formation/disappearance of interfaces	Replacement of interfaces
1.	Adhesional wetting	LAI disappears	SAI replaced by SLI
2.	Spreading wetting	LAI forms	SAI replaced by SLI
3.	Immersional wetting	No change in LAI	SAI replaced by SLI

Liquid-vapor interfaces (LVI), solid-liquid interfaces (SLI), and solid-vapor interfaces (SVI).

**Figure 19.1** The surface tensions relevant, mechanism of film formation: (a) Contact, (b) Spreading and solvent evaporation, (c) Film formation] and types of wetting in the film coating process.

Process variables influencing wetting mechanism are summarized in Table 19.2 [12].

19.3 Functions of the Polymeric Coating

There are three types of coatings concerning the function of the coat, like nonfunctional, functional, and active coatings. Non-functional coatings are meant for improving compliance. Majority of the functional coatings can modify (delay release) or prolong the drug release apart from masking the bad taste/odor. Inactive coatings, drug layer (coating layer), will be deposited on to the inert substrate. These kinds of coatings are mainly applied to avoid the interaction of different drugs and also to merge different release characteristics in one dosage forms. Different polymers used

Table 19.2 Process variables influencing the wetting mechanism.

S. no	Type of variable	Factors
1.	Substrate related	a) Chemical properties of the drug b) Physicochemical properties of dosage form like strength; size/shape; surface properties, etc. c) Hydrophobicity d) Core polymer interactions e) Surface roughness f) Porosity
2.	Coating formulation related	a) Particle size b) Plasticizer c) Viscosity d) The solubility of coating polymer
3.	Coating process variables	a) Atomizing air pressure b) Type of spray c) Solvent evaporation rate d) Temperature and/or Humidity e) Distance between spray gun and substrate f) Post coating curing g) Droplet momentum

for protection and masking are given below in the following Tables 19.3 to 19.6 [13].

19.3.1 Application of Film Coating in Modified Release System (Enteric Release)

Enteric coating also called as gastro-resistant coating, have been used widely from mid of 19th century to resist the release of drug in stomach in order to protect the drug material from the acidic environment of stomach and also to target the release at specific intestinal segments [14]. This also helps from the irritating effect of few drugs. All these can be achieved by coating with the weak acid enteric polymers, which were in unionized form at the acidic pH and ionized form at higher alkaline pH of intestine. To target the different sections of intestinal segments, polymers were designed with different pH thresholds as shown in Table 19.7 [13, 15].

Table 19.3 Different aqueous soluble polymers for protection and taste masking.

Manufacturer	Trade name	Polymer
Colorocn	Opadry	PVA
Ashland Aqualon	Oxycellulose Natrosol	HEC
BASF	Kollidon Kollicot IR Kollicot IR protect	PVP PVA-PEG copolymer PVA-PEG: PVP
Wolff cellulosics	Walocel	Na CMC
Bio Grund	Aquapolish	PVA-PEG copolymer
Down chemical	Methocel	HPMC
Wolff cellulosics	Walocel	
Sensient	Spectracel	
Shin-Estu	Pharmacoat	

Table 19.4 Entero-soluble cationic polymers for protection and taste masking.

Manufacturer	Trade name	Polymer
Evonik	Eudragit E, E PO, E 12.5	Amino domethyl methacrylate copolymer
BASF	Kollicoat, Smart seal 30 D	

These polymers coated layer will get dissolve only after reaching to the lower GIT, where pH is more than their dissolution pH threshold [16]. Conversely, the in vivo performance of enteric-coated products largely depends upon several gastrointestinal physiology variables such as gender, feeding status, transit time, and gastrointestinal pH [17, 18]. Various polymers like CAP, HPMCP, PVAP, and hydroxypropyl methylcellulose acetate succinate (HPMCAS) and methacrylic acid copolymers, etc., can be used for delay release. Numerous solid dosage forms like pellets, tablets, microcapsules, etc., can be coated with these enteric polymers to achieve the required benefits. Extensive research has been done to coat the tablets by making use of several polymers like Eudragit L-30 D-55, Eudragit L-30 D-55 HPMCP, CAP, Acryl-EZE®HPMC-55, and Ethyl cellulose, etc.

Table 19.5 Enteric anionic polymers for protection and taste masking.

Manufacturer	Trade name	Polymer
Eastman	Cab Eastman	CAB (Cellulose acetate butyrate)
	Kollicoat MAE 30 DP/100 P Eastacryl 30 D NF Eudragit L 30 D-55/L 100-55	Type A Methacrylic acid copolymer
	Eastman C-A-P NF	CAP
	Eudragit L 100	Type B Methacrylic acid copolymer
Evonik	Eudragit L 100	Type B Methacrylic acid copolymer
	Eudragit FS 30 D	Methacrylic acid copolymer
	Eudragit S 100 Eudragit S 12, 5	Methacrylic acid copolymer, Type C
FMC biopolymers	Aquacoat CPD	CAP
	Keltone LV CR	Sodium alginate
SSB Pharma	SSB 55	Shellac
Aqualon	Akucell	CMC

Hard gelatin capsules can be coated with non-aqueous solutions of Eudragit E, L, and S 12.5 for lower GIT targeted delivery. Coated capsules are gained their importance because of the independency of coating composition on capsule filling [19].

19.3.2 Liposomal Coating

The retention time of liposomes can be increased by surface modification with fewer uptakes by RES. The polymer coating is an alternative method for this. The liposomal coating is a simple process of mixing liposome

Table 19.6 Insoluble polymers used for protection and taste masking.

Manufacturer	Trade name	Polymer
BASF	Kollicoat SR 30 D	PVA
Evonimk	Eudragit RS 30 D, RS 100/RS PO, RS 12.5	Ammonio methacrylate Type B: Poly(ethyl acrylate-co-methyl methacrylate-co-trimethylamminoethyl methacrylate chlorid) 1:2:0.2
	Eudragit RL 30 D, RL 100/RL PO, RL 12.5	Ammonio methacrylate Type A: Poly(ethyl acrylate-co-methyl methacrylate-co-trimethylamminoethyl methacrylate chlorid) 1:2:0.2
	Eudragit NM 30 D	Poly (ethyl acrylate-co-methyl methacrylate) 2:1
	Eudragit NE 30 D	Poly (ethyl acrylate-co-methyl methacrylate) 2:1
Eastman	Eastman CA	Poly (ethyl acrylate-co-methyl methacrylate) 2:1
Colorcon	Surelease	Cellulose acetate
FMC	Aquacoat	Ethyl cellulose
Dow chemical	Ethocel	Ethyl cellulose

suspension with that of polymer solution. In this, there will be no chemical linking of the polymers to the lipid molecules of liposome. As reported by Hirofumi Takeuchi [20], there is a feasibility of coating the surface of liposomes with modified hydrophilic polymers such as PVA or PAA

Table 19.7 Threshold pH with target site of GIT.

S. no	pH thresholds	Target site in GIT
1.	~5–5.5	Duodenum
2.	~6	Jejunum
3.	~7	Ileum and Colon

(polyacrylic acid) having a hydrophobic anchor (s) (PVA-R or PAA-R). The residence time of these liposomes in the biological system can be increased by coating of liposomes with mucoadhesive polymers and thus enhancing the oral bioavailability of the drug [21]. Oral absorption of peptide drugs has been enhanced by chitosan-coated liposomes [22–24]. Other polymers that have been employed in the surface coating of liposomes include amylopectin, dextran, and pullulan [25].

19.3.3 Aerosol Coating

Aerosol performance of micronized drugs in carrier excipient drug blends was improved by excipient coating. Daniela Traini [26] investigated this use in the dry powder inhalers. Both EC (ethylcellulose) and PVP were used as coating agents. Carriers were prepared via sieve fractioning followed by spray drying, with and without polymer additive. After blending for 24 h, each coated and uncoated blended systems (salbutamol sulphate-SS) were evaluated for particle size, drug-carrier adhesion, morphology, and aerosolization performance. Particle adhesion between SS and aerosol performance (fine particle fraction; FPF) followed the rank: PVP coated > uncoated > EC coated lactose. Enteric coating of different dosage forms with enteric polymers are given in Table 19.8.

19.4 Polymeric-Coating Approaches to Targeted Colon Delivery

Colon-targeted drug delivery has been gained importance from many years owing to its prospective to progress the treatment of some of the local diseases like Ulcerative colitis (UC) and Crohn's disease (CD) and irritable bowel syndrome (IBS) and minimizing systemic side effects. A higher concentration of drug will reach to colon with negligible systemic absorption or without being absorbed in upper part of GIT. Enhancement of absorption of several drugs can be seen owing to longer retention of colonic content and colonic content nature and making this organ as an ideal site for drug delivery. A drug can be delivered to the colon via the oral, or the rectal route, among that oral route is most preferred than rectal due to their convenience [4]. Major approaches for targeting colon have been given in Table 19.9.

Table 19.8 List of polymers for the enteric purpose of several dosage forms.

S. no	Dosage form	Drug	Polymers used	Ref
1.	Tablets	Diclofenac and Prednisone	Blend of cellulose esters and enteric polymers (CAP, E L 100, HPMC-HP 55)	27
2.	Pellets	Duloxetine hydrochloride	HPMC P, HPMC ASMG, and HPMC ASMF	28
3.	Tablets	Esomeprazole magnesium trihydrate	HPMCP, Eudragit L-30 D-55, CAP	29
4.	Pellets	Duloxetine hydrochloride	Acoat® AS-LF, Eudragit® L30D55 HPMCP-HP55.	30
5.	Tablets	Azithromycin Dihydrate	EC, Eudragit L-30 D-55, HPMC-55,	31
6.	Pellets	Duloxetine hydrochloride	Acoat® AS-LF, Eudragit® L30D55 HPMCP-HP55.	32
7.	Tablets	Rabeprazole	Hydroxypropyl methyl cellulose-Phthalate CAP	33

(Continued)

Table 19.8 List of polymers for the enteric purpose of several dosage forms. (*Continued*)

S. no	Dosage form	Drug	Polymers used	Ref
8.	Capsules	Omeprazole	Methyl acrylic acid and ethyl acrylate	34
9.	Tablets	Prednisolone	Eudragit1 L 30 D-55. HP-DD	35
10.	Tablets	Diclofenac sodium	Hydroxypropyl methylcellulose (HPMC) E3 Eudragit L 100 Eudragit E 100	36
11.	Capsules	Paracetamol	HPMCAS-LF, Eudragit L100-55 and HP-55	37
12.	Tablets	Pantoprazole	CAP Eudragit L100	38
13.	Tablets	Ilaprazole	Eudragit L 100 HPMC P 50	39
14.	Tablets	Zileuton	Eudragit L- 100 Ethylcellulose Eudragit S-100	40
15.	Pellers	Budesonide	Eudragit s 100	41
16.	Tablets	Lansoprazole	Eudragit® L100-55:	42

(Continued)

Table 19.8 List of polymers for the enteric purpose of several dosage forms. (*Continued*)

S. no	Dosage form	Drug	Polymers used	Ref
17.	Solid lipid nanoparticles	Enrofloxacin	Polyacrylic resin II	43
18.	Microsponges	5-FU	Eudragit S100/Eudragit L100 blend of EdS100	44
19.	compressed enteric coated pellets	-	Eudragit FS 30 D, Eudragit L30 D-55	45
20.	Microspheres	Duloxetine	Eudragit L-100	46
21.	Microporous Osmotic pump tablet	Quetiapine fumarate	HPMCP	47
22.	Microspheres	5 FC	Eudragit-S-100 Eudragit- L-100	48
23.	Tablets	Rifampicin and isoniazid	EudragitR L30D-55	49
24.	Microparticles	Cinnarizine	Eudragit® L100-55	50
25.	Nanoliposomes	Alendronate Sodium	Eudragit L100	51

(Continued)

Table 19.8 List of polymers for the enteric purpose of several dosage forms. (*Continued*)

S. no	Dosage form	Drug	Polymers used	Ref
26.	Microparticles	Biochanin A	Ethyl cellulose	52
27.	Microcapsules	Rabeprazole sodium	EC, HPMCK100M Eudragit L100	53
28.	Solid Lipid Nanoparticles	Alendronate sodium	Eudragit S100	54
29.	Microcapsules	Astaxanthin	Alginate gelatin	55
30.	Nanoparticles	5-fluorouracil	Eudragit S-100	56
31.	Tablets	Didanosine	HPMCP 5.5	57
32.	Nanoparticles	-	HPMC PVP, PVA-PEG, HPC	58
33.	SNEEDS	Insulin	Eudragit1 L100	59
34.	Liposomes	Sildenafil	Chitosan solution HPMC	60
35.	Osmotic pump capsule	Sinomenine hydrochloride	HPMCP HP 50, HPMCP HP 55. Eudragit L 100	61
36.	Tablets	Prednisolone	Zein and Kollicoat® MAE 100P	62

Table 19.9 Major approaches for targeting colon drug delivery [63].

Colon targeted drug delivery-Approaches			
Approach		Basic feature	
I. Chemical Approaches	i. Azo conjugates	The drug is conjugated	via an azo bond
	ii. Cyclodextrin conjugate		with cyclodextrin
	iii. Glycoside conjugate		with glycoside
	iv. Glucuronide conjugate		with glucuronate
	v. Dextran conjugate		with dextran
	vi. Polypeptide conjugate		with polypeptide
	vii. Polymeric prodrug		to the polymer
II. Pharmaceutical Approaches			
1. Polymeric coating			
	i. Film Coating by using pH-sensitive polymer	Coating with enteric polymers releases drug only at alkaline range	
	ii. Film Coating by using biodegradable polymer	After reaching the colon, degradation of polymer layer can be seen because of colonic bacteria action, followed by drug release.	
2. Embedding in matrices			
	i. Embedding in biodegradable polysaccharides	Swelling and biodegradable action can be seen with the polysaccharides and drug embedded in the matrices will be released.	
	ii. Embedding in pH-sensitive matrices	The pH-sensitive polymer will degrade in the target area of GIT and results in the release of drug content.	

(Continued)

Table 19.9 Major approaches for targeting colon drug delivery [63]. (*Continued*)

Colon targeted drug delivery-Approaches	
3. Timed released systems	
4. Redox-sensitive polymers	
5. Bioadhesive system	Substrates coated with the bioadhesive polymer which selectively gives the adhesion to the colonic mucosa.
6. Coating of microparticles	The Drug should get a release through the semipermeable membrane
7. Osmotic controlled delivery	Osmotic pressure

19.4.1 Enzymatically Degradable Film Coatings [64]

19.4.1.1 *Film Coatings Based on Naturally Occurring Polysaccharides*

Naturally occurring polysaccharides of animal, plant, algal or microbial origins such as chondroitin, pectin, chitosan, amylase, and galactomannan are widely used for colon delivery owing to their susceptibility to colonic degradation, safety, biocompatible nature, and also implications as food additive.

19.4.1.2 *Film Coating on the Basis of Synthetic Azo Polymers*

The probability of colon targeting by the utilization of azo reductive bacterial activities was first time used for the development of oral administration of peptide delivery. Dip coating was done by using copolymers of styrene and hydroxyethyl methacrylate (HEMA) (1:6), which is cross-linked with 1% or 2% of divinyl azobenzene. These were dissolved in methylene chloride or chloroform with methanol at concentration of 20 % v/v.

Hard gelatin capsule (size 5) containing bovine insulin was coated with film-forming material such as copolymer of HEMA and styrene cross-linked with substituted divinylazobenzene derivative. Copolymers of HEMA and methyl methacrylate (MMA), or elseterpolymers of the latter compounds and methacrylic acid, were prepared by using substituted

divinylazobenzenes as azo cross-linkers and applied, as ethanolic solutions, to size 9 hard-gelatin mini capsules containing various tracer molecules, such as fluorescein, caffeine, ibuprofen, and theophylline.

19.4.2 pH-Sensitive Film Coatings

19.4.2.1 *Film Coating on Basis of Enteric Solubility of Polymers*

For targeting the colon, pH-sensitive film coatings were widely exploited, especially by using polymethacrylates. These materials having the enteric solubility nature, eg, Eudragit L (having the solubility at pH above 5.5 or 6.0) and Eudragit S (with higher dissolution pH threshold of 7.0), are widely used from many years.

19.4.2.2 *Film Coatings on the Basis of Acid Solubility of Polymers*

Acid soluble pH-responsive film coatings were also used apart from enteric for colon targeting. This will be coupled with gastro-resistant layer and will be normally expecting to dissolve as a result of direct or indirect microbial fermentation activity of flora present in the caecum and ascending colon areas.

19.5 Natural Polymers Applications in Modified Release Dosage Forms

Modified release oral solid dosage forms afford many specific advantages in drug release pattern in contrast to conventional drug delivery systems. Natural polymers are of special interest in formulating these delivery systems because of their safety, biodegradability, rich sources, and biocompatibility. Structure of the natural polymers could also be modified to achieve the desired effect [65]. Typically, cellulose-based carriers provided many choices for formulators in solid oral modified-release dosage forms such as matrix tablets and pellets [66, 67]. However, despite the fact that some natural polymers and modified natural polymers have been included in the pharmacopeia, the applications of most natural polymers in solid oral modified-release dosage forms need to be further explored and an updated review on the recent advances in this field is essential. Few examples of natural polymers for modified release are given in Table 19.10 [68].

Table 19.10 Modified-release dosage forms based on modified chitosan.

Polymer	Drugs	Dosage forms/description
Modified Chitosan S-protected thiolated chitosan	Antide	Coated matrix tablets Increase mucoadhesive properties, improve the bioavailability of peptides, using Eudragit L 30 D-55 as the coating material
Pectin based Physical mixtures of pectin-hypromellose	–	Compression coated tablets, scintigraphic evaluation of tablets in healthy volunteers
Physical mixtures of pectin-Comritol* 888 ATO	Mesalamine	Compression coated tablets, Box-Behnken experimental for optimization of formulations
Physical mixtures of pectin- hydroxyethylcellulose	Rhubarb	Matrix coated with Eudragit S 100 for further retarding the drug release
Guar gum-based polymer	Omdazole, Metronidazole	Dry coating (compression coating) <i>In vivo</i> evaluation in healthy volunteers
Guar gum-based polymer	Prednisolone	Dry coating (compression coating), <i>In vivo</i> gamma scintigraphic study in human volunteers
Guar gum-based polymer	Flurbiprofen	Dry coating (compression coating), <i>In vivo</i> study in healthy volunteers

*Compritol® 888 ATO is glyceryl behenate

19.6 Application of Polymer Coating in Biomedicine

Biomedicine (medical biology) is a branch of medical science that applies physiological and biological principles to clinical practice. It has been the dominant health system for more than a century. The use of

polymer coatings in the field of biomedicine can be categorized on basis of its application as follows; i) orthopedic materials, ii) cardiovascular stents, iii) anti-bacterial surfaces, iv) drug delivery, v) biosensors, and vi) tissue engineering. These polymer coatings majorly help to improve the mechanical strength, to enhance biocompatibility, for electrical conductivity, protection from deterioration, electrical conductivity, and to tailor the surface chemistry of compounds. Magnesium and its alloys are having vast fracture toughness, compressive yield strengths, low density, and similar elastic moduli relative to bone [69]. Despite the fact that magnesium and alloys are widely used materials for implants, but there is a need to reduce their corrosion rate. Luo *et al.* [69] used poly(3,4-ethylenedioxythiophene) (PEDOT) polymer by electropolymerization technique. Dexamethasone was incorporated into the liquid ionic electrolyte. The formed coating was lessened the rate of corrosion. Failures in orthopedic implants are because of poor osteointegration and bacterial infection. Indomethacin was incorporated along with biodegradable and anti-bacterial polymers (chitosan and PLGA) by modifying the Ti surfaces with titania nanotube (TNT). Delivering drugs to the bone for extended time has also been reported [70]. Growth factors were incorporated along with antibiotics to prevent infections and promote bone healing [71]. Application of polymer coating on other areas was given in Table 19.11.

19.7 Pellet Coating (Film Coating and Dry Coating)

Pellets serves as an excellent coating substrate owing to i) low surface area to volume ratio compared to powders and granule, ii) higher concentrations of active substances can be incorporated without forming large-sized particles, iii) high degree of flexibility in product development, and iv) therapeutic advantages such as division of dose strength, modification of drug release.

19.7.1 Pellets by Solution/Suspension Layering

Pellets can be prepared by solution or suspension layering using fluid bed granulators, coating pans, and Wurster coaters. Certainly, all the formulation components are dissolved or suspended during the solution or suspension layering.

Table 19.11 Biomedical applications of polymer coatings [72].

Area of application	Polymer used	Description
Orthopedic material		
	poly(L-lactide) (PLLA) coatings	To increase its cytocompatibility and also to reduce corrosion rate Mg and its alloys.
	HA (hydroxyapatite) doped PLA (polylactic acid)	To decrease the corrosion rate of AZ31 Mg alloy
	alginate and poly(L-lysine)	For the controlled delivery of growth factors
	PLA	Layers of Mg alloy AM 50 and Ca-P and/or Cap-P-Mg minimized the corrosion rate and promoted cell attachment.
Cardiovascular stents		
	PLA-poly(ethylene glycol) (PEG)	Short term long term toxicity of carbon nanotubes was reduced and also their aggregation was also prevented.
	poly(ethylene carbonate)	Stainless steel stents are spray-coated to reduce their toxicity
	PEDOT	To promote adsorption of HSA, cell adhesion and cytocompatibility,
	The copolymer of L-Lactide which is immobilized with heparin and methyl benzyloxy carbonate in THF (tetra hydro furan)	Degradation time for coated bare metal stunts was maintained for 16 weeks and only very little inflammation was observed in <i>in vivo</i> conditions.

(Continued)

Table 19.11 Biomedical applications of polymer coatings [72]. (*Continued*)

Area of application	Polymer used	Description
Antimicrobial surfaces		
	Antimicrobial PU coatings	Shown good adhesion strength, mechanical properties. The bacterial activity was to 95% and signifying their importance in the implants as a coating material.
	poly(1,3- <i>bis</i> -(<i>p</i> -carboxyphenoxy propane)- <i>co</i> -sebacic anhydride) 20:80	Coated films were effective against <i>E.coli</i> and <i>S. aureus</i> population and also shown CR drug delivery. This can confirm their application in developing catheters and implants.
	PCL/PLA polymers with polypropylene meshes.	Post implantation infection risk was minimized.
Drug delivery		
	hydroxypropylmethylcellulose (HPMC) and carboxymethylcellulose (CMC);	Prepared spray-coated microneedle patches can be potentially used the vaccine and intradermal delivery of pharmaceutical compounds.
	Poly methacrylic acid and chitosan	Drugs can be effectively loaded into microspheres by mesoporous silica nanoparticles.

(*Continued*)

Table 19.11 Biomedical applications of polymer coatings [72]. (*Continued*)

Area of application	Polymer used	Description
Tissue engineering		
	Bio degradable polymers-PU, PCL, PLGA. PCL.	The proliferation of chondrocytes (cartilage cells) on poly(dopamine)-coated tissues
	PGA, PLLA, PDLA along with some synthetic degradable polymers	bone tissue engineering (BTE)
	poly[2-(methyl acryloyl oxy) ethyl dimethyl-(3-sulfopropyl) ammonium hydroxide] (PMEDSAH)	Long-term growth of human embryonic stem (hES) cells are observed in different culture media
Biosensors		
	Coating of PAPBAOT on the glassy electrode of carbon. (poly(3-aminophenyl boronic acid-co-3-octylthiophene))	Enzyme-free glucose sensor was developed.
	Poly styerene co polyacrylic acid	Polymers imprinted with proteins were prepared. These will show the antibody-like specificity.

The droplets were impinged on to the substrates after spraying of coating formulation and spread on their surfaces, followed by drying phase. During the drying phase, dissolved materials will crystallize and forms the solid bridge between core and initial layer of drug substances and also between the successive layers. This will continues till the required layers of API is formed and the potency of pellets can be achieved.

19.7.2 Dry Coating

Apart from the coating of pellets, tableting of coated particles also gained importance from 1960s [73, 74]. Various aspects of compression of pellets

such as type and amount of coating material, cushioning excipient, and compression forces are widely discussed in the literature [75, 76]. Breakage of coating, changes in quality of product in terms of dissolution are the main drawbacks of tableting of pellets. The “soft tableting” approach is used by using relatively elastic/cushioning excipients in order to minimize the damage during compression [78]. Ethylcellulose can be notably used in the compression of coated pellets because of its cushioning property; it can minimize the damage [77]. All the pharmacopoeial conditions such as uniformity of weight and content, friability, hardness, and dissolution profiles must meet during the compression of coated pellets. All these specified conditions make the formulation of coated pellets as an extremely complex process. With these specified reasons, very few compressed pellets have reached the market like a prolonged-release formulation with metoprolol [79], an enteric-coated formulation with omeprazole (Antra[®] MUPS), and similar theophylline (Theo-Dur[®]), lansoprazole (Prevacid[®]) and esomeprazole (Nexium[®]) products.

19.8 Conclusion

Broad research endeavors have been made in the past to coat various dosage forms with different natural and synthetic polymers. Film coating is an excellent choice for formulation development procedures where it is useful in playing diverse roles. Taste masking or protection forms the external environment, which are simple examples of effectively used approaches. The film coating can be achieved through the use of water-soluble, cationic, anionic, or neutral insoluble polymers from different chemical structures. Enteric polymers are used to restrict the release of drug in the upper GIT. Polymer coatings in the field of biomedicine have been used widely to improve the mechanical strength, to enhance biocompatibility, for corrosion protection, electrical conductivity, and to tailor surface chemistry.

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