

Rheology of Polymer Blends and Nanocomposites

Theory, Modelling and Applications

Edited by

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Knowledge is like a river. Its nature is to constantly flow. Wherever it can flow, it does so, nourishing culture. On the other hand, the same knowledge, if devoid of values becomes a source of destruction for the world. When values and knowledge become one, there can be no more powerful instrument for the welfare of humankind. Today, physicists have even begun investigating the possibility that the essential substratum of the manifest universe and the individual are one and the same. We are standing on the threshold of a new era wherein material science and spirituality will move forward hand in hand.

Sri Mata Amritanandamayi Devi

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Preface

“Rheology,” defined as the study of flow and deformation, predates its formal introduction by Professor Bingham in 1929. Chinese philosophers Confucius (551–479 BCE) and Heraclitus (540–475 BCE) have described “flow” in philosophical contexts. In the book of Judges (Old Testament), Deborah, “Prophetess of God,” stated that “the mountains melted/flowed before the Lord.” Thus, rheology is often malaproposed as theology. Rheology, primarily dealing with three concepts: kinematics, conservation laws, and constitutive relations, received significant academic attention in the last 30 years.

By considering the enormous volume of data available, it is purely utopian to have a single book dealing with all diverse aspects of rheology. Because of space constraints, the authors have tried to limit the choice of references, and a great number of publications have not been mentioned/cited. This book is designed to provide an updated information on applications of rheology, rheological techniques along with the opportunities and challenges in the study of rheological properties of polymer blends and nanocomposites.

The first chapter is designed to provide a general introduction to rheology and various terms involved in rheology of polymer blends and nanocomposites. Chapter 2 (Rheology of polymer blends) details the rheological properties of different types of polymer blends. Chapter 3 discusses the characterization of interfaces in polymer blends and nanocomposites using rheology. This chapter details the different theoretical models and their application in polymer blends and nanocomposites. Chapter 4 details the rheological properties of colloids. Chapter 5 discusses the rheological properties of polymer nanocomposites. Chapter 6 reviews the rheological properties of polymer-clay nanocomposites. This chapter introduces the various theoretical models used and their application in the characterization of polymer-clay nanocomposites. Chapter 7 is designed to deliver the rheological properties of polymer blend nanocomposites. Chapter 8 provides an updated information on rheological properties of heavy crude oil-asphaltene nanocomposites blends. Chapter 9 describes the rheology of hydrogels. The rheological properties of liquid crystalline polymers have been detailed in Chapter 10. Chapter 11 provides a critical evaluation on Rheo-SAXS. Chapter 12 discusses the advancements in the field of Fourier transform rheology. Chapter 13 evaluates the magneto rheological properties of polymer nanocomposites.

We would like to thank all the authors (for providing contributions) as well as the publisher (Elsevier publishing company). Their experience, expertise, and enthusiasm were the key for successful completion of this project. We sincerely hope that this book will aid the reader in exploring new frontiers (beyond what is presented here) and might serve as a comprehensive guide to the latest developments in the field of rheology.

Dr. Sarathchandran C

Introduction to rheology

1

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Abstract

The current chapter is designed to provide a general introduction to rheology. This is accomplished by explaining various terms involved in rheology, different types of rheological response exhibited by various materials, and different sets of rheological geometries commonly used for various studies.

Keywords: Deborah number; Non-Newtonian behavior; Reynolds number; Rheology; Stress–Strain response; Viscoelastic materials.

1. Introduction

Rheology is the branch of physics that describes the deformation and flow of materials thereby interrelating force, deformation, and time. The term “*rheology*” is derived from Greek word “*rheo*” meaning “*flow*” and logia indicating “the study of.” This term was coined by Professor Bingham in 1920 from a Greek quotation “*Panta rai*” meaning everything will flow. In 1678, Robert Hooke developed the “*True Theory of Elasticity*” and proposed that tension on a spring is proportional to its extension (Barnes et al., 1989). Later, in 1678, Sir Isaac Newton published “*Principia*” where due attention was given to liquids. Thus, rheology covers the behavior of perfectly viscous liquid (Newtonian fluid) materials and ideal solid (Hookean solid) materials. Rheological behavior is best illustrated using silicone material nicknamed “*Bouncing Putty*.” When this material is extended quickly, it undergoes brittle failure (characteristic of solids), while on long time scale it flows and finds its level when placed in a container (characteristic of liquids). Thus, solid/liquid response from a given material depends on the time scale of experiment or deformation process. This introduces “*Deborah number*” (D_e) defined as the ratio of characteristic time of material under consideration to the characteristic time of experiment,

$$D_e = T/\tau \quad (1.1)$$

where, τ is the characteristic time of material and T is the characteristic time of experiment. Higher value for D_e corresponds to solid materials, while lower value

for D_e corresponds to liquid materials. In a Hookean solid, stress is directly proportional to strain and is best explained by the spring model, while for a Newtonian liquid, stress is directly proportional to strain rate and can be explained using the spring and dashpot model. However, certain class of materials show a combination of viscous and elastic properties and are called viscoelastic materials. Their properties are illustrated using different combinations of spring and dashpot. In a Hookean solid, stress and strain are in phase, while in a Newtonian liquid, stress and strain are out of phase, whereas in a viscoelastic material, there is a phase lag between stress and strain (refer Fig. 1.1) (Mills, 2007).

Thus, for a viscoelastic material,

$$\sigma(\omega, t) = G' \gamma \sin(\omega t) + G'' \gamma_0 \cos(\omega t) \quad (1.2)$$

Here, G' and G'' are storage modulus and loss modulus, respectively. Lissajous plots show the variation of stress and strain. Fig. 1.2 shows the Lissajous plot for elastic, viscous, and viscoelastic materials.

Viscoelastic materials can be divided into four categories depending on the fluid viscosity response to the duration and magnitude of applied shear rate (Fig. 1.3).

- (a) Pseudoplastic: This is the most common type of non-Newtonian behavior observed. Rheological profile for shear thinning liquids shows three characteristic regions. Low viscosity plateau at high shear rates which gives infinite shear viscosity (η_∞). This is followed by a sharp increase in viscosity with decreasing shear rate. This region called shear thinning region can be described mathematically using power law model. At low shear rate, a second plateau region of constant viscosity can be observed. This is called the zero shear viscosity (η_0). In certain materials, the viscosity shows a dramatic increase (attaining values close to that of solids) below certain critical stress. In such cases, η_0 will be absent and this type of response is called plastic flow. Pseudoplastic behavior arises due to microstructural rearrangement taking place in the direction of applied shear.

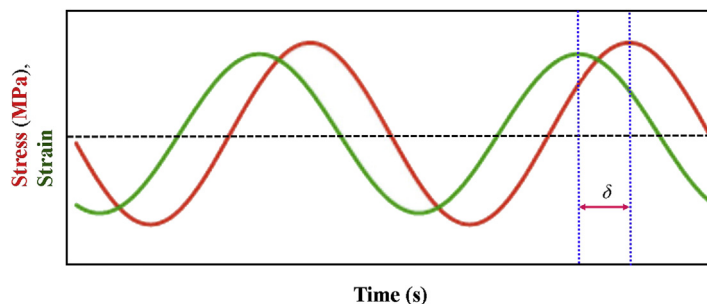
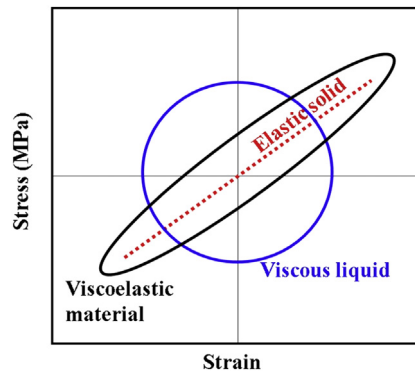
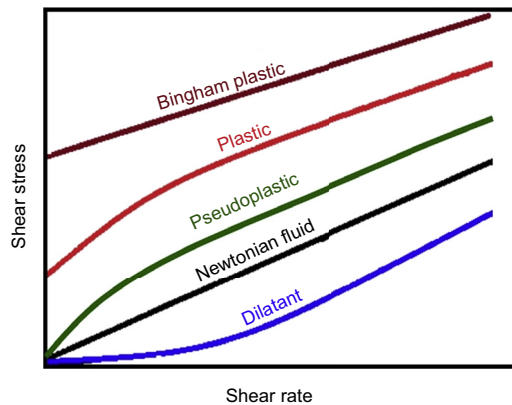


FIGURE 1.1

Stress–Strain response for a typical viscoelastic material with a phase lag of δ

**FIGURE 1.2**

Lissajous plots for elastic, viscous, and viscoelastic materials.

**FIGURE 1.3**

Different categories of non-Newtonian behavior.

- (b) **Dilatant:** Shear thickening fluids or dilatant fluids show an increase in viscosity with increase in shear stress/shear rate. The relation between shear stress and shear rate will be nonlinear, and shape of curve will be convex with zero intercept. These fluids/suspensions tend to reorder on application of shear rate so as to reduce the shear force. However, the fluid will not get enough time to reorganize on application of high shear rate leading to significant buildup of shear force. Dilatant property depends on concentration, shape/size of dispersed particles, and density. ([Maranzano and Wagner, 2001](#)).
- (c) **Thixotropic fluids:** In Newtonian, pseudoplastic and dilatant fluid viscosities are independent of time, while there are certain fluids which show a time-dependent shear thinning and shear thickening behavior. In thixotropic fluids, viscosity decreases with time under constant shear conditions or thixotropic

fluids show time-dependent shear thinning behavior and the property arises due to rupture of intermolecular bonds. This brings out the significance of “yield stress” defined as the minimum stress required to initiate flow. Patton introduced thixotropic index defined as

$$I = \sigma_1 / \sigma_2$$

where σ_1 is the shear stress before shearing and σ_2 is the shear stress after shearing, both the values taken at low shear rates.

- (d) Rheopectic fluids show a time-dependent increase in viscosity which arises due to aggregation/association of particles during shear, reversible cross-link formation, etc.

Certain fluids behave as solids at low shear force and show Newtonian characteristics above certain critical shear force. Such fluids are called Bingham fluids.

Non-Newtonian fluids do not exhibit a linear relationship between shear stress and shear strain. A certain threshold stress must be applied to initiate flow.

Rheology is also used in the study of complex fluids like mud, body fluids, polymer solutions, food, mixture of fluids, emulsions, etc. Exploring the flow properties of liquid involves investigating the response of individual fluid molecules in response to applied stress followed by determining the variation of fluid’s velocity field as a function of position and time. There are two main flow regimes: (a) laminar and (b) turbulent.

1.1 Laminar flow

A type of streamlined flow of single-phase fluids in which the fluid moves in parallel layers, or laminae. The layers flow smoothly over each other with instabilities being damped by the viscosity (refer Fig. 1.4).

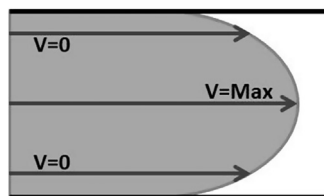
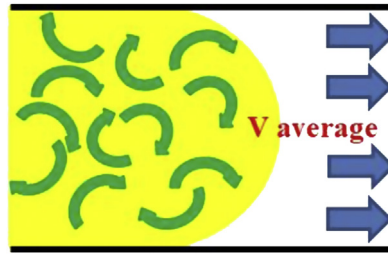


FIGURE 1.4

Schematic representation of laminar flow.

**FIGURE 1.5**

Schematic representation of turbulent flow.

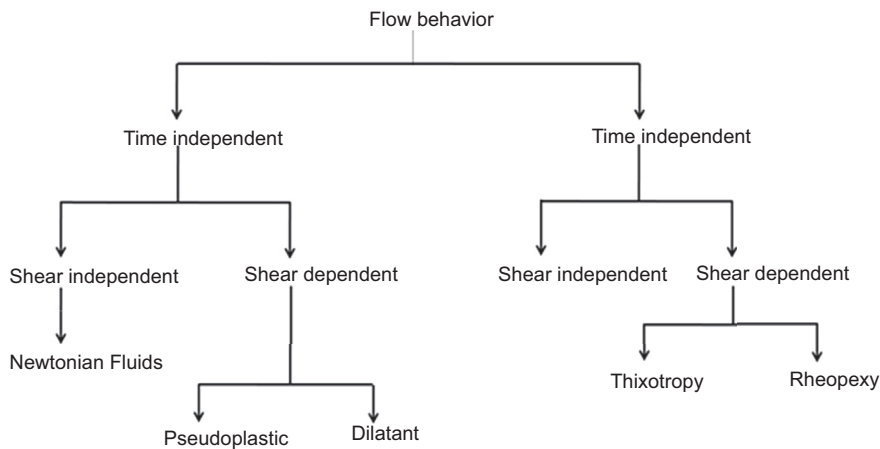
1.2 Turbulent flow regime

A fluid flow regime characterized by swirling/chaotic motion as the fluid moves along the pipe or conduit. Investigation of the flow properties in this regime is highly complicated (refer Fig. 1.5).

Study of flow properties introduces a dimensionless number called Reynolds number (Re), which is defined as the ratio of change in momentum due to acceleration (usually called inertial effects) to the change in momentum due to frictional forces called viscous effects.

$$Re = \left(\frac{\rho V l}{\eta} \right) \quad (1.3)$$

where ρ is the density, η is the fluid viscosity, V is velocity, and l is the characteristic length. Small value for Re indicates the domination of viscous effects, while large value points to negligible viscous effects. Fig. 1.6 shows a schematic representation of the different types of flow behavior shown by various materials.

**FIGURE 1.6**

Schematic representation of different types of non-Newtonian flow behavior of various materials.

2. Stress control and strain control rheometers

Investigation of the influence of sinusoidal stress or sinusoidal strain input on a complex fluid requires careful understanding of the working principle of modern rheometers. Rheometers can broadly be divided into stress controlled and strain controlled. In strain controlled rheometers, input is a nonsinusoidal strain (usual nomenclature is calculated strain) and the output is a sinusoidal stress (usually known as measured stress) (Bae et al., 2013) and can probe higher frequencies. In stress controlled rheometers, input is a sinusoidal stress (usual nomenclature adopted is the given stress) and the output is a nonsinusoidal strain (usually known as measured strain). They are based on drag cup motor first used in Deer rheometer built in 1968 and have better torque sensitivity.

3. Different rheometer geometries

Depending on the characteristics of material being tested and information required, a wide range of measuring geometries are available each of them specially designed to achieve optimum results. Disc spindles can be used to study the viscosity of wide variety of liquids, while cylindrical spindles are useful to study the shear stress, shear rate, and viscosity of non-Newtonian fluids, whereas vane spindles can be used to study the viscosity of gels. Similarly Couette cells offer good sensitivity to low viscous fluids and fluid suspensions. However, parallel plate, cone, and plate geometries are commonly used in the study of polymeric materials. Fig. 1.7 shows the different rheometer geometries commonly used in polymer industry.

Consider a fluid placed between two parallel plates of area $A \text{ cm}^2$ and separated by a distance $d \text{ cm}$ as shown in Fig. 1.8.

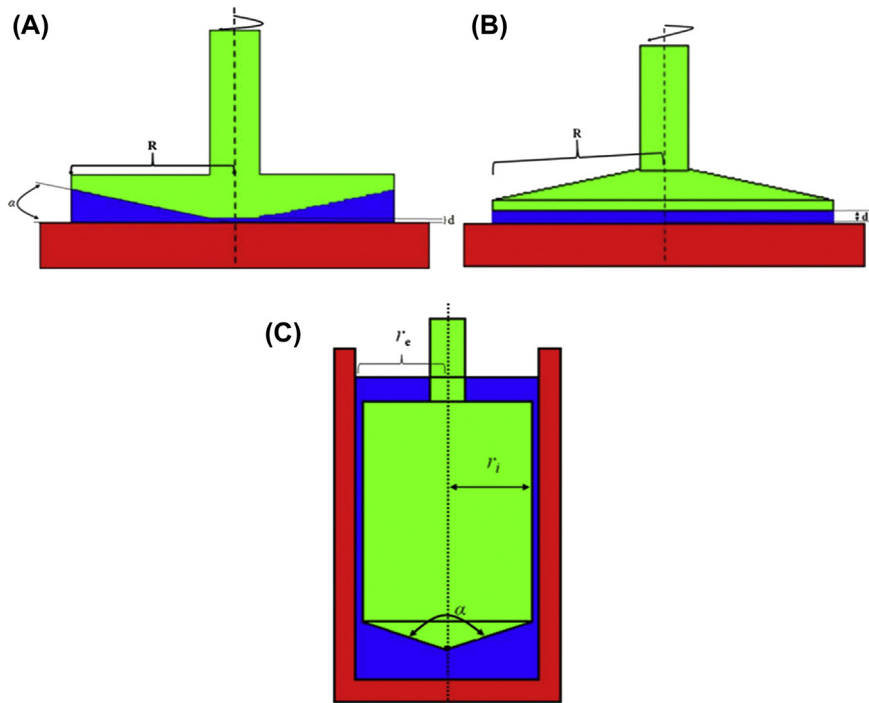
Let the laminar shear force applied on upper movable plate be $F \text{ dynes} \cdot \text{cm}^{-1}$ and the constant velocity attained be $v \text{ cm} \cdot \text{s}^{-1}$, then the fluid layers have a velocity gradient between zero and $v \text{ cm} \cdot \text{s}^{-1}$. Then,

$$\text{Shear stress } (\sigma) = \text{Force/Area} = F/A \text{ dynes cm}^{-1}$$

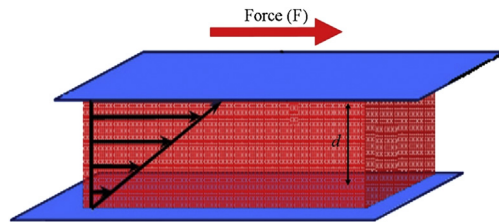
$$\begin{aligned} \text{Shear rate (defined as the ratio of velocity to distance between the plates)} (\gamma) \\ = v/d \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Coefficient of viscosity (ratio of shear stress by shear rate)} (\eta) \\ = \sigma/\gamma \text{ dyne} \cdot \text{s} \cdot \text{cm}^{-2} \end{aligned}$$

In oscillatory shear experiments, a sinusoidal strain ($\gamma_0 \sin(\omega t)$) is applied on the sample and corresponding stress response ($G' \gamma_0 \sin(\omega t) + G'' \gamma_0 \cos(\omega t)$) is recorded and used to calculate complex shear modulus (G^*), where G' and G'' are the real and imaginary parts of G^* . G' (storage modulus) provides the response of material which is in phase with the applied stress/strain and is related to the elastic

**FIGURE 1.7**

Rheometer measuring geometries (A) cone and plate, (B) parallel plate, and (C) Couette cell.

**FIGURE 1.8**

Schematic representation of force applied on a fluid placed between two parallel plates.

component, while G'' (loss modulus) provides the response which is out of phase with the applied stress/strain and is related to the viscous component of the material. The ratio G''/G' is called loss tangent or tan delta ($\tan \delta$) and provide the ratio of elastic to viscous response of the material under consideration.

3.1 Rheology of miscible polymer blends

Different experimental methods are used to investigate the miscibility of polymer blends, such as differential scanning calorimetry (DSC), dynamic mechanical thermal analysis, dielectric measurement, cloud point measurement, microscopy, small-angle X-ray and neutron scattering, fluorescence technique, etc. Each of these experimental methods can only probe the homogeneity/heterogeneity in a polymer blend at a certain scale range. Thus, the determination of the miscibility in polymer blends depends on the resolution limit of the experimental method(s) employed. For instance, DSC analysis is the most widely accepted technique to determine the miscibility in polymer blends by determining glass transition temperature T_g . Numerous investigators reported the rheological behavior of miscible polymer blends without specific interaction. The polymer blend systems investigated include (Yang and Han, 2008).

Poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA).

(He et al., 2003; Colby, 1989)

PMMA and poly(styrene-*co*-acrylonitrile) (PSAN) (Zuo et al., 2005, 2006;

Bousmina et al., 2002; Aoki, 2008; Zheng et al., 2001)

PMMA and poly(vinylidene fluoride) (PVDF) (Nicotera et al., 2006;

Zhang et al., 2012, 2013; Salaeh et al., 2018)

PS and poly(vinyl methyl ether) (PVME), 16–28 (Kitade et al., 1994;

Takahashi et al., 1994; Madbouly and Ougizawa, 2004)

PS and poly(R-methylstyrene) (PRMS) (Kim et al., 1998)

Polyisoprene (PI) and poly(vinylethylene) (PVE), 29–32 (Trask and

Roland, 1989; Arendt et al., 1997; Chung et al., 1994; Roland and Ngai, 1991)

Liang et al. studied rheological properties of polyether sulfone/polyimide blends, the increment of the complex viscosity and the elastic modulus of the blends with respect to the composition. For blends containing more than 10 wt% polyimide, sudden changes in the rheological properties were observed at temperatures above the phase boundary due to phase separation and/or cross-linking (Liang et al., 1992). Mani et al. reported the influence of phase separation on linear viscoelastic response for miscible blends of polystyrene (PS) and poly(vinyl methyl ether) with a lower critical solution temperature (Mani et al., 1992). Roovers' and Toporowski studied the rheological properties of blends of 1,3-polybutadiene (7% 1,2) and 1,2-polybutadiene (63% of 1,2 polybutadiene) (Roovers and Toporowski, 1992). Varughese reported the melt rheological behavior of miscible blends of plasticized poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR). He concluded that the higher melt viscosity of blends as compared with plasticized PVC suggests better melt processability of the latter. For high-ENR blends, the melt elasticity becomes temperature independent for any value of shear stress when the parameters such as principal normal stress difference and elastic shear modulus are considered (Varughese, 1990). Recently, Iqbal et al. reported the time–temperature superimposed master curves of PE/OPE blends, the formation

of relaxed polymer chains with increasing OPE loading, and the blends exhibited positive deviation from the Rouse dynamics at higher frequencies were observed (Iqbal et al., 2016).

3.2 Rheology of immiscible polymer blends

Rheological behavior of an immiscible polymer blend, consisting of two homopolymers, two random copolymers, or a homopolymer and a random copolymer, depends on its morphological state, which in turn depends on different factors such as blend composition, mixing condition (temperature, the intensity of mixing, duration of mixing) employed, and type of mixing device hired.

When blending two immiscible homopolymers (or random copolymers), two types of phase morphology have been observed: dispersed two-phase morphology and cocontinuous morphology and the major factors that control blend morphology, which in turn control the rheological behavior of immiscible polymer blends; they are (1) thermodynamic factor, (2) interfacial tension, and (3) hydrodynamic factor. One can produce polymer blends via rapid precipitation from a solution without the influence of hydrodynamic variables, while hydrodynamic variables play a very important role in melt blending. It should be mentioned that the interfacial tension can be decreased considerably, and thus decreasing the sizes of the discrete phase, by using an effective compatibilizing agent.

Hedegaard et al. reported that extensional viscosity of polyethylene (PE) and polylactic acid (PLA) is employable in determining co-continuous compositions, blend stability, and the size scale of phase domains in order to control co-continuous morphologies (Hedegaard et al., 2015). The rheology and the flow-induced morphology of in situ compatibilized PP/PS blends were investigated by Huo et al. (Huo et al., 2007). The effect of copolymer addition on the rheological behavior of a binary mixture of PS and high-density polyethylene (HDPE) has been reported by Iza et al. and they found that the deformation and the relaxation of the domains are completely modified by the presence of compatibilizers at the interface (Iza et al., 2001). Kang et al. reported that all PLA/PP blend ratios exhibit non-Newtonian and shear-thinning characteristics in the range of the applied shear rates. They examined the storage modulus, dynamic loss modulus, and complex viscosity curves for pure PLA, pure PP, and PLA/PP blends with different components as a function of frequency. There is a clear dependence of complex viscosity on PP content: complex viscosity increases with increasing PP content (Kang et al., 2015). Silva et al. discussed the rheological proprieties of immiscible polyamide-6 (PA-6) and ethane-propene rubber (EPM) blend with compatibilizing agent EPM-g-MA with high viscosity, and elasticity ratios were studied and claim that oscillatory shear, uniaxial extension, and stress relaxation experiments (in both shear and extension) showed the existence of one relaxation time for the immiscible blend (Silva et al., 2007). Vinckier et al. investigated and provided better insight in the relation between droplet deformation of polyisobutene

and polydimethylsiloxane (PDMS) blends and experimental data compared with Doi–Ohta theory (Vinckier et al., 1997).

Numerous reports are available on the rheological behavior of immiscible polymer blends with and without the presence of compatibilizers. iPP/EPR (Orazio et al., 1993), poly(lactic acid) (PLA)/poly(butylene adipate-*co*-terephthalate) (PBAT) (Al-Itry et al., 2014), PC/PET (Carrot et al., 2007), HDPE/PS (Martin et al., 2000), PE/PA12 (Moan et al., 2000), PDMS and polyisoprene (PI) (Gavvani et al., 2018), poly(styrene)/poly(methyl methacrylate) (Panxianhu et al., 2017), and polylactide/poly(vinylidene fluoride) (PLA/PVDF) (Salehiyan et al., 2018) being some of them.

3.3 Rheology of polymer composites

Polymer composites consist of a thermoplastic polymer forming the matrix phase and a large amount of inorganic particles or fibers, which are often referred to as particulate-filled polymers. Polymer composites are developed to attain a set of properties not possessed by a polymeric matrix alone. There are numerous industrial products made of particulate-filled polymeric materials: polymers filled with mica or calcium carbonate, carbon black (CB)—filled elastomers, thermoplastic polymers, or thermosets reinforced with glass fibers or carbon fibers. When inorganic fillers or glass fibers are added to a polymer, the resulting material exhibits a complex rheological behavior, quite different from the rheology of neat homopolymers. Generally, it is well known that the addition of fillers to a molten polymer increases the melt viscosity and decreases the melt elasticity. The volume fraction of the particles as well as other factors, such as the shape of the particles, the particle size and size distribution, and the state of dispersion of the particles are known to influence the *bulk* rheological properties of particulate-filled polymer melts.

George et al. incorporate pineapple leaf fiber to low-density polyethylene (LDPE) and investigated the effects of the fiber loading, fiber length, chemical treatments, and temperature on melt viscosity. Shear stress–temperature superposition was also done to predict the melt viscosities of the composite materials (George et al., 1996). The effects of relative composition of sisal and glass fibers in LDPE, shear rate, and temperature on the melt viscosity of these composites were investigated by Kalaprasad et al. They found that viscosity of glass fiber system shows stronger interaction compared to sisal fibers and power law equation was used for the pseudoplastic behavior of hybrid composites (Kalaprasad et al., 2003). Samsudin et al. examined the effects of the surface treatment of filler with stearic acid on the rheological properties of the PP hybrid composite highly filled with the CaCO_3 and talc. They found that shear viscosities decrease with increasing shear rate and also observed the increment in the fluidity and better dispersion attained by the surface treatment of CaCO_3 particles with stearic acid. In hybrid composite, the shear viscosity decreases with increasing temperature (Samsudin et al., 2006). Song et al. filled CB in HDPE and ethylene tetrafluoroethylene and study the

time-temperature-concentration superposition principle to understand the linear rheology of filled polymers (Song et al., 2009).

Rheological study of some of the particle or fiber-filled polymers are PS/CB (Song et al., 2017; Cao et al., 2010), Nylon 6/Mica (Bose and Mahanwar, 2005), PDMS/mica (Jia et al., 2013), glass fiber (GF)/poly-(ethylene-co- α -octene) POE (Wang et al., 2016), polypropylene/hemp fiber (Twite-kabamba et al., 2009), short bamboo/glass fiber/polypropylene (Nayak et al., 2009), sisal fiber/PS (Nair et al., 2000), and HDPE/sisal fiber (Mohanty and Nayak, 2007).

Polymer nanocomposites are an interesting and emerging area in industries and academic field. Compared with the composites, nanocomposites exhibit enhanced desired properties with very low amount (1-5 wt%) of nanofillers. Here, we are focusing your attention toward the rheological properties of polymer nanocomposites.

Maio et al. examined the rheological effect of the PLA hybrid systems (PLA 4032D and PLA 2003D) with different surfactant-modified nanoclays (Cloisite 30B and NanofilSE3010). The extensional viscosity, and strain hardening behavior, in particular, NSE3010-hybrids showed a marked extensional thickening, whereas the stronger polar interactions between the phases in PLA hybrid-C30B determined increments in elongational viscosity, but inhibited the strain hardening behavior (Maio et al., 2015). Linear viscoelastic response of the single-walled carbon nanotube-filled poly(methyl methacrylate) (PMMA) nanocomposites was studied by Du et al. By varying nanotube loadings, significant influence was observed particularly at low frequencies, which specify the influence of nanotubes on polymer relaxation dynamics at length scales longer than the entanglement distance (Du et al., 2004). Kim et al. examined the influence of surface modification of CNTs on the linear viscoelastic response was examined by measuring dynamic shear viscosity, storage modulus, loss modulus, and extensional flow behavior of CNT/epoxy composites and compared with the unmodified CNT-filled epoxy (Pathak et al., 1998). They found that surface treatments of CNTs provided more homogeneous dispersion and stronger interaction between the CNT and the polymer matrix results higher storage and loss moduli and shear viscosity compared to the untreated CNTs. Kota et al. reported rheological percolation in PS/MWNT nanocomposites and observed that the storage modulus exhibited a low-frequency plateau at concentrations exceeding 2 vol% that suggests the formation of a pseudo-solid-like network of percolated MWNTs (Kota et al., 2007).

A number of reports have been published on the rheological properties of polymer nanocomposites: polypropylene (PP) (Li et al., 2003; Gu et al., 2004; Lee et al., 2008; Jian et al., 2003; Kiziltas et al., 2018; Wang et al., 2018) poly(ethylene oxide)/silica (Zhang and Archer, 2002), poly(ϵ -caprolactone)/clay (Lepoittevin et al., 2002), PS-clay (Zhao et al., 2005), polycarbonate (PC)/multiwalled carbon nanotubes (MWNTs) (Potschke et al., 2004), and HDPE/clay (Swain and Isayev, 2007), linear low-density polyethylene/clay (Swain and Isayev, 2007), epoxy/clay (Swain and Isayev, 2007), and PS/clay (Kim et al., 2002).

Recently, researchers are concentrated to examine different properties of blend nanocomposites (polymer blend is considered as whole matrix and introduce nanofiller into the matrix). Moussaif and Groeninckx studied the rheological properties of miscible PVDF/PMMA/organoclay blend nanocomposites. They introduced both hydrophilic and organophilic nanofillers into the blend matrix and found that PVDF/PMMA nanocomposites exhibit a solid-like behavior at lower frequency indicating the formation of a percolated network structure. 10 wt% of PMMA in PVDF/PMMA nanocomposites is considered as the optimal concentration (Moussaif and Groeninckx, 2003).

Rheological percolation threshold of MWNT incorporated PP/NR blend has been investigated by Thankappan et al. Different loading of MWNT on different composition (80/20, 50/50, 20/80) of PP/NR blend were compared with PP/MWNT composites and found that rheological percolation threshold of MWNT-filled PP/NR (80/20 and 50/50 blend ratio) was found to be lower than that of MWNT-filled PP. They also found “double percolation” phenomenon particularly in 50/50 composition (Thankappan et al., 2015).

Rheological properties of hydrophilic and hydrophobic SiO₂-filled PS/PVME blends were studied by Xia et al. The results proposed that the preferential attraction between PS and hydrophobic SiO₂ is weaker than PVME and hydrophilic SiO₂ (Xia et al., 2013).

4. Conclusion

In this section, we have provided a general introduction to rheology, different types of rheometers, and various rheometer geometries commonly used. These concepts are important in understanding the rheological properties discussed in other chapters.

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Rheology of polymer blends

2

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Abstract

Polymer blends are physical mixtures of two or more homopolymers or copolymers. This type of materials have wide spectrum of technological applications, and their properties are influenced, e.g., by the properties of single components and morphology of final material. The rheology of polymer blends is connected with the processing of polymer blends and is influenced by thermodynamics, morphology, and their evolution during testing. This chapter provides an overview of research areas in the field of miscible and immiscible polymer blend rheology. Selected issues were discussed, e.g., application of time-temperature superposition principle in miscible polymer blends (concerning influence of intra- and intermolecular hydrogen bonding), influence of rheometer geometry on the obtained results, multiphase flow (including behavior of droplets in matrix), and flow imposed morphologies.

Keywords: Immiscible polymer blends; Miscible polymer blends; Polymer blends; Rheological properties; Rheology.

1. Introduction

Polymer blends can be defined as mixtures of two or more polymers that have been blended together to create a new material which combines specific properties (unique for each component separately). Blending of polymers is a relatively fast way to obtain materials. From a thermodynamic point of view, polymer blends are classified as miscible (homogenous) or immiscible (heterogeneous)—however, most polymers are immiscible. One of the most important factors related to the properties of immiscible polymer blends is a compatibility between polymer phases, which can be improved by suitable compatibilizers (responsible for reducing interfacial tension). The rheology of polymer blends is influenced by thermodynamics, morphology, and their evolution during testing.

The morphology of the immiscible polymer blends is affected by the composition of blend, mixing conditions (like temperature, intensity, and duration of mixing), and type of mixing device. The morphology of obtained polymer blend affects the rheological behavior of polymer blend, and there are three major factors

that permit to control morphology of polymer blend: thermodynamic factor, interfacial tension, and hydrodynamic factor.

The miscibility of polymer blends can be investigated using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMA), small-angle X-ray scattering, small-angle neutron scattering, scanning and transmission electron microscopy, magnetic resonance spectroscopy, and others. Mentioned methods permit to investigate a homogeneity (or heterogeneity) of polymer blend system at a certain scale range. The most used methods are DSC and DMA, which are useful for determining the glass transition temperature of the polymer blend system, and when a single glass transition temperature is observed, the polymer blend is expected to be miscible.

The blending of two immiscible polymers can be performed using a batch-type mixing device (e.g., Brabender or Banbury mixer) or a continuous mixing device (e.g., twin screw extruder). In accordance to the blending techniques, two types of phase morphology can be obtained, i.e., dispersed two-phase morphology and co-continuous morphology.

The Gibbs free energy of mixing depends on enthalpic and entropic contributions:

$$\Delta G_m = \Delta H_m - T \cdot \Delta S_m$$

where ΔG_m is the free energy of mixing, ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing (negligible for the high molecular weight materials like polymers), and T is the absolute temperature.

For the miscible polymer blends (characterized by homogeneity on the molecular level), Gibbs free energy of mixing is negative and close to enthalpy of mixing due to specific interactions ($\Delta G_m \approx \Delta H_m \leq 0$). In the case of immiscible polymer blends (characterized by the phase separated morphology), ΔG_m is positive and close to ΔH_m ($\Delta G_m \approx \Delta H_m \geq 0$).

Two types of polymer blend behavior can be observed, i.e., upper critical solution temperature (UCST) behavior (e.g., polystyrene/poly(α -methylstyrene) blend) and lower critical solution temperature (LCST) behavior (e.g., polystyrene/poly(vinyl methyl ether) blend). When the temperature increases, the miscibility of UCST-type polymer blend increases, whereas the miscibility of LCST-type polymer blend decreases. In some polymer blends, combined UCST and LCST phase behavior is observed.

The rheological models of miscible polymer blends involve solutions and mixture of polymer fractions (homologous polymer blends (HPBs)). In the case of immiscible polymer blends, basic simple models like emulsions or suspensions are used. The compatibilized polymer blends can be analyzed in the context of block copolymer models. In accordance to the literature, there are some great works that cover theoretical and experimental aspects of polymer blend rheology (Han, 2007; Utracki, 2011; Utracki and Kamal, 2003).

The investigation of rheological properties of polymer blends involves mainly determination of **steady shearing flow properties**—i.e., shear stress (σ_{12}), viscosity

(η), and first normal stress difference (N_1) as functions of shear rate ($\dot{\gamma}$)—using cone-and-plate rheometer, capillary or slit rheometer, and **oscillatory shearing flow properties**—i.e., dynamic storage modulus (G') and loss modulus (G'') as functions of angular frequency (ω) at various temperatures—using cone-and-plate rheometer. It is also possible to determine the elongational flow properties for polymeric fluids (Dealy and Wissbrun, 1999). The details connected with the experimental methods for measurement of rheological properties of polymer blends are presented in the literature (Han, 2007).

This chapter provides an overview in the area of rheology of miscible and immiscible polymer blends. Some general trends and experimental findings presented in the literature are described.

2. Rheology of miscible polymer blends

HPBs can be defined as mixtures of fractions of the same polymer having the same chemical constituting units (mers) characterized by different molecular mass distribution. This kind of polymer blends is miscible because of narrow molecular mass distribution. In this context, any polydispersed polymer can be classified as HPB. Han (1988) analyzed dynamic viscoelastic properties (using logarithmic plots of dynamic storage modulus G' vs. loss modulus G'') of binary blends of nearly monodisperse polybutadienes, polystyrenes, and poly(methyl methacrylate)s. The relationships between the rheological properties and the molecular weight distribution of homologous polymer were studied by few authors (Masuda et al., 1970; Bersted and Slee, 1977; Franck and Meissner, 1984; Fuchs et al., 1996; Ressia et al., 2000; Fujiyama et al., 2002).

The rheological properties of several miscible polymer blends are described in the literature, for example, for poly(methyl methacrylate)/poly(styrene-co-acrylonitrile) (Wu, 1987; Pathak et al., 1998; Aoki and Tanaka, 1999), ultra-high molecular weight polyethylene (UHMWPE)/linear low-density polyethylene (LLDPE) (Vadhar and Kyu, 1987), poly(methyl methacrylate)/poly(styrene-co-acrylonitrile) (Yang et al., 1994), poly(methyl methacrylate)/poly(vinylidene fluoride) (Yang et al., 1994), poly(ethylene oxide)/poly(methyl methacrylate) (Colby, 1989), polyisoprene/poly(vinyl ethylene) (Roland and Ngai, 1991), polystyrene/poly(vinyl methyl ether) (Ajji et al., 1988), polystyrene/poly(α -methylstyrene) (Kim et al., 1998), poly(4-vinylphenol)/poly(ethylene oxide) (PVPh/PEO) (Cai et al., 2003), and polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) (PS/PPO) (Cai et al., 2003).

The miscibility of polymer blends is affected by temperature and polymer blend composition, and the equilibrium phase diagram permits to describe miscibility (or immiscibility) of polymer blend system. The miscible polymer blends have generally negative values of the Flory–Huggins interaction parameter χ (segmental interaction parameter), which means that in analyzed polymer blend system attractive interactions are presented. In the case of immiscible polymer

blends, the Flory–Huggins parameter is positive, which suggest that polymer blend has repulsive interactions.

Han and Kim (1989a), (1989b) presented the molecular theory for the linear viscoelasticity of miscible polymer blends. The Flory–Huggins parameter χ is very important during the analysis of composition dependence of linear viscoelastic properties of miscible polymer blends. This theory predicts positive deviations from linearity in the plots of zero-shear viscosity versus blend composition for the polymer blends characterized by very small negative values of Flory–Huggins parameter, and negative deviations from linearity for the polymer blends characterized by large values of Flory–Huggins parameter. These predictions are confirmed by the literature for the PVDF/PMMA blends and PMMA/PSAN blends. The Han and Kim theory can be used when the glass transition temperature of both components is similar, molecular weight distribution is narrow, and the relationships between the segmental interaction parameter and blend composition and temperature are known.

The time-temperature superposition (TTS) can be applied to flexible homopolymers to estimate rheological properties at various temperatures. In the case of miscible polymer blends, the effectiveness of TTS is limited. The TTS works in some polymer blends, which are characterized by the very small difference between the T_g of both components. Failure of TTS in miscible polymer blends observed by several authors can be caused by dynamic heterogeneity (which is related to the difference in glass transition temperatures of the polymer blend components), presence of two components characterized by the different relaxation dynamics (the relaxation time of the polymer with higher T_g has stronger temperature dependence than this observed for polymer with lower T_g), and difference of friction coefficients (Han, 2007).

Generally, for miscible polymer blends, TTS fails due to presence of dynamic heterogeneity connected with presence of concentration fluctuations. The plots of storage modulus versus loss modulus can be used as a tool for determining applicability of TTS for miscible polymer blends. Yu and Zhou (2012) considered the rheology of miscible polymer blends with viscoelastic asymmetry and concentration fluctuation and proposed new model to describe such systems.

The rheological properties of polymer blends should be also concerned in the terms of interactions presented in the system. Some polymer blends have weak interactions, whereas in other ones specific interactions are presented (e.g., hydrogen bonding). Yang and Han (2008a) investigated the linear dynamic viscoelasticity of several miscible polymer blends with hydrogen bonding (confirmed by FTIR spectroscopy), i.e., poly(vinylphenol)/poly(vinyl acetate), poly(vinylphenol)/poly(vinyl methyl ether), poly(vinylphenol)/poly(2-vinylpyridine), and poly(vinylphenol)/poly(4-vinylpyridine). Spectroscopic analysis (by FTIR method) confirmed presence of intramolecular and intermolecular interactions in investigated systems. It has been found TTS is applicable to all PVPh-based miscible polymer blends, including the PVPh/PVME blend, which is characterized by large difference (199°C) between glass transition temperatures of components. Gaikwad et al., 2010 investigated the

miscible polymer blends of poly(vinyl methyl ether) (PVME) with poly(styrene) (PS), poly(styrene-*stat*-vinylphenol) (PSVPh) copolymers, and poly(vinylphenol) (PVPh). The amount of hydrogen bonding was controlled by using copolymers characterized by different vinylphenol content. The failure of TTS was observed for PS/PVME and PSVPh/PVME blends, whereas the TTS was successful for PVPh/PVME systems and PSVPh/PVME blends with higher vinylphenol content (despite high difference between the glass transition temperatures of single components). Obtained results showed that there exists some “critical concentration” of hydrogen bonds, which is necessary to restore the applicability of TTS. The rheological behavior of miscible polymer blends with presence of specific interaction was also studied by [Cai et al. \(2003\)](#) for poly(4-vinylphenol)/poly(ethylene oxide) (PVPh/PEO) blend, [Yang and Han \(2008b\)](#) for blends of hydrogenated functional polynorbornene polycarbonate and poly(2-vinylpyridine).

Failure of TTS in miscible polymer blends was reported for poly(ethylene oxide)/poly(methyl methacrylate) ([Colby, 1989](#)), polyisoprene/poly(vinyl ethylene) ([Roland and Ngai, 1991](#)), polystyrene/poly(vinyl methyl ether) ([Ajji et al., 1988](#)), and polystyrene/poly(α -methylstyrene) ([Kim et al., 1998](#)).

3. Rheology of immiscible polymer blends

Rheological behavior of immiscible polymer blends is connected with their morphology, and a lot of works are connected with investigation of the morphology–rheology relationship. Moreover, it is well known that the evolution of polymer blend morphology occurs during the mixing process (testing and processing of immiscible polymer blends). This is a very complex issue, which is covered by only few works and should be further investigated.

A lot of works considered rheological properties of immiscible polymer blends, e.g., polystyrene/low-density polyethylene ([Utracki and Sammut, 1988](#)), linear low-density polyethylene/low-density polyethylene ([Utracki and Schlund, 1987](#); [Müller et al., 1994](#)), poly(methyl methacrylate)/polyethylene ([Martinez and Williams, 1980](#)), polyisoprene/polydimethylsiloxane ([Kitade et al., 1997](#)), polystyrene/linear low-density polyethylene ([Lee and Park, 1994](#)), polystyrene/poly(methyl methacrylate) ([Wang and Lee, 1987](#); [Graebbling et al., 1993](#)), and polyoxymethylene/copolyamide ([Ablazova et al., 1975](#); [Tserbenko et al., 1974](#)).

It should be also pointed out that the rheological properties of immiscible polymer blends are affected by the geometry of the applied rheometer, so the results obtained using cone-and-plate rheometer will not overlap this obtained using capillary or slit rheometer. It was shown by [Han et al. \(1995a\)](#) that plots of steady shear viscosity versus shear rate for PMMA/PS blends obtained from a cone-and-plate rheometer do not overlap those obtained from a capillary rheometer. The same situation was observed for the two microphase-separated triblock copolymers: a polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer and a polystyrene-*block*-polyisoprene-*block*-polystyrene copolymer ([Han et al., 1995b](#)). Moreover,

Frayer and Huspeni (1990) found that the plots of viscosity versus shear rate of thermotropic liquid-crystalline polymers obtained from a slit rheometer were significantly different from those obtained from a capillary rheometer.

In the immiscible polymer blends, the drop size and their distribution (connected with the applied blending method) affects the rheological properties of obtained systems. In the case of extrusion process at the same shear stress, the larger L/D ratio permits to obtain smaller droplets in matrix in comparison with smaller L/D ratio. It should also be pointed out that immiscible polymer blends during extrusion process (i.e., flowing through a long cylindrical tube) are characterized by the presence of many drops with different degrees of deformation. Han and You (1971a), (1972) perform the microscopic analysis of the extruded parts of 20/80 HDPE/PS blend and found that the drops are larger near the center of the tube in comparison with the drops presented near the edge of the tube, whereas the higher deformation of drops are observed for the ones near the tube. This phenomenon is related to the fact that the shear stress increases from the center of the tube and reaches maximum value at the tube wall, so the higher deformation degree of drops is observed near the tube wall.

During the mixing process drop deformation, breakup, coalescence, and migration can be observed. In accordance to the literature, the most investigated (theoretically and experimentally) are drop deformation and drop breakup (e.g. Taylor, 1934; Cox, 1969; Choi and Schowalter, 1975; Chin and Han, 1979; Chin and Han, 1980; Torza et al., 1972, Millikan and Leal, 1991; Olbright and Kung, 1992; Cristini et al., 2003). From the technological point of view, the most important is breakup (or coalescence) of multiple drops in pressure-driven flow. In the nonuniform shear flow (e.g., pressure-driven flow), the very complicated morphologies can be obtained, e.g., lamellar morphology (Subramanian and Mehra, 1987; Lohfink and Kamal, 1993) or fibrillation (Champagne et al., 1996; Kim et al., 1997). Multiphase flow in the polymer processing is well described in the literature (Han, 1980, 1981).

One of the interesting phenomena in the area of immiscible polymer blends is large extrudate swell, where extrudate swell is generally described as an effect of relaxation of polymer chains after leaving from die. The large extrudate swell is the effect of deformed drop recoil, which occurs in extrudate of dispersed two-phase blend extruded through a cylindrical tube. The increasing deformation of drop inside the die is connected with the increasing of extrudate swell (Han, 2007). This phenomenon was described and investigated by Han and Yu (1971b) for high-density polyethylene (HDPE)/polystyrene (PS) blends. Authors investigated the effect of polymer blend composition on extrudate swell ratio (d_j/D), where d_j is extrudate diameter and D is capillary diameter. The measurements were performed at 200°C using capillary die characterized by L/D of 4, where L/D is the ratio of length to diameter of the capillary die. Further investigations focused were similar but L/D was 4, 12, and 20 (Han and Yu, 1972). In the analyzed polymer blends, the amount of HDPE was equal to 20, 50, and 80 wt.%. In the 20/80 and 50/50 HDPE/PS blends, polystyrene was continuous phase, while HDPE forms a drop phase. The largest extrudate swell (the largest deformation of HDPE drops

inside the die) was observed for the 20/80 HDPE. The increasing of shear stress (i.e., increasing of extrusion rate) was connected with the increasing extrudate swell ratio, so the deformation of drops was also increasing.

Steady shearing and oscillatory shearing flow properties of polymer blends, presented as plots of first normal stress difference (N_1) versus shear stress (σ_{12}), and logarithmic plots of storage modulus (G') versus loss modulus (G''), can be used for determining the rheological compatibility of polymer blends. [Chuang and Han \(1984\)](#) investigated compatible (two low-density polyethylenes (LDPE) having different values of molecular weight, poly(methyl methacrylate)/poly(vinylidene fluoride)) and incompatible (poly(methyl methacrylate)/polystyrene) polymer blend. They found that plots of first normal stress difference versus shear stress and plots of storage modulus (G') versus loss modulus (G'') for the LDPEs blends become temperature- and blend composition-independent, while for the PMMA/PVDF blend only temperature-independency was observed. For the analyzed incompatible polymer blends, mentioned plots were temperature-independent. [Han and Chuang \(1985\)](#) investigated four compatible (i.e., blends of two different grades of low-density polyethylene, poly(vinylidene fluoride)/poly(methyl methacrylate), poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene, and poly(styrene-co-acrylonitrile)/poly(styrene-co-maleic anhydride) and two incompatible (polyamide 6 with poly(ethylene-co-vinyl acetate) and ethylene-based multifunctional polymer) polymer blends. Authors found that obtained results (in the form of N_1 vs. σ_{12} and G' vs. G'' plots) are temperature- and blend composition-independent for the compatible polymer blends, while for the incompatible polymer blend temperature-independent and composition-dependent correlations are observed. [Han and Yang \(1987\)](#) found that for the compatible polymer blends of poly(styrene-co-acrylonitrile) (SAN) and poly(ϵ -caprolactone) (PCL), the logarithmic plots of N_1 versus σ_{12} and G' versus G'' plots become virtually independent of temperature, but vary regularly with blend composition.

4. Summary

The rheology of polymer blends is influenced by thermodynamics, morphology, and their evolution during testing. Rheology of immiscible polymer blends is more described in the literature than rheology of miscible polymer blends. It is due to the fact that nowadays immiscible polymer blends (including compatibilized polymer blends) have greater technological importance. The analysis of complex systems, like polymer blends, is complicated, especially in the terms of further processing of these materials, which can be realized by several different ways (using different machines under different conditions). The most important issue that should be concerned is rheology—morphology processing relationship in the area of polymer blends. The experimental investigations should be connected with theoretical consideration of obtained systems (development of suitable theoretical models), which will be useful during the rheological behavior modeling.

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Interfacial characterization of immiscible polymer blends using rheology

3

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Abstract

The morphology and ultimate properties of polymer blends depend on (1) polymer structure, (2) blend composition, (3) interfacial tension (which depends on structure and additives), (4) rheology, and (5) processing. Most polymer blends are immiscible giving rise to a coarse morphology, weak adhesion between phases, and in some cases poor mechanical properties. Rheology of immiscible polymer blends usually disobey the classical rules and needs to be studied with other theories specially designed for biphasic systems. Here, we discuss various theories developed over the years for immiscible polymer blends, especially dealing with the interfaces. Greatest challenge of the simple Palierne model in explaining the experimental results obtained for blends with special type of morphology can be dealt with the modified form developed.

Keywords: Immiscible polymer blends; Interfacial interaction; Interfacial tension; Polymer structure; Rheology.

1. Introduction to polymer blends

Polymer blending is one of the most effective and economic methods to combine the properties of different polymers (Utracki and Utracki, 2003). Thus, blending two different polymers aims the following: (1) combining the properties of different polymers, (2) cost reduction, improvement in material processing, etc. Polymer blends can be broadly divided into two categories (Utracki and Utracki, 2003), (Thomas et al., 2013)

1. Miscible polymer blends: Miscible polymer blends are homogenous at the molecular level, where the miscibility arises due to specific interactions between the blend components (miscibility arising due to entropy contribution has been reported). Miscible polymer blends are associated with a negative free energy of mixing ($\Delta G < 0$). Common examples are shown in Table 3.1.
2. Immiscible polymer blends are heterogeneous mixtures of two different polymers. They are associated with a positive free energy of mixing ($\Delta G > 0$).

Table 3.1 Conditions of miscibility, along with common examples for miscible and immiscible polymer blends.

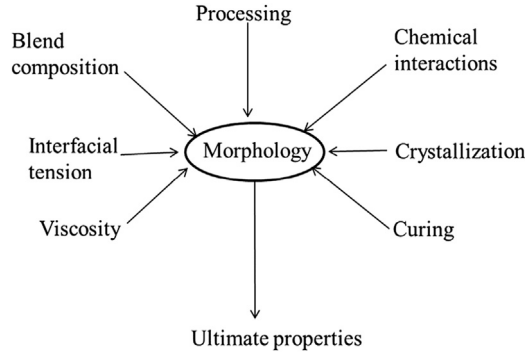
Miscible blends	Immiscible blends
Homogenous	Complete phase separation
Mechanical properties of components averaged	Synergistic mechanical properties
$\Delta G < 0, \left(\frac{\partial^2 \Delta G}{\partial \phi^2} \right)_{T,P} > 0$	$\Delta G > 0$
They show a single glass transition temperature	They show the separate glass transition temperatures of the component polymers
Common examples include polystyrene(PS)-polyphenylene oxide(PPO), poly(ethylene terephthalate)(PET)-poly(butylene terephthalate (PBT), poly(methyl methacrylate) (PMMA)-poly(vinylidene fluoride) (PVDF)	Most of the polymer blends are immiscible

Studies show that in the case of miscible polymer blends, improvement in properties follow the additivity rule, whereas in the case of immiscible polymer blends, a synergistic improvement in properties can be obtained. This makes immiscible polymer blends an area of intensive research for academic and industrial basis. Table 3.1 shows the conditions for miscibility, along with common examples for miscible/immiscible polymer blends.

It is generally accepted that blending of two different polymers result in a third phase usually called the interphase formed due to interdiffusion/compatibilization (Aji and Utracki, 2003). The thickness of the interface varies between 2 and 60 nm. Li et al. (1999) measured the interface of PC-SAN blends to map the miscibility region (Li et al., 1999). Figure 3.1 shows the significance/effect of interfaces on the ultimate properties of polymer blends.

2. Rheology as a tool to study the interface of polymer blends

Rheology as a tool to characterize and study the interface of polymer blends is widely accepted (Utracki and Kanial, 1982). Immiscible polymer blends are considered as colloids or suspensions in the molten state, and the particles change their shape under shear stress (T. and Moldenaers, 2002). Small amplitude oscillatory shear and large amplitude oscillatory shear are used for the investigation (Hyun et al., 2002, 2011; Vega et al., 1998). Thereby, the interdependence between rheological behavior of melts and morphology plays a key role in the optimization of

**FIGURE 3.1**

Significance of morphology with various factors that influence the morphology and thereby the ultimate properties.

properties (Freischmidt et al., 2001), (Chen et al., 2005). Thus, the interfacial tension between the melts is an important parameter that characterizes the extent of reaction. Various theories like self-consistent field theory (Rubinstein and Colby, 1988), mean field theory (Paul, 2012; des Cloizeaux, 1988; Ganesan and Pryamitsyn, 2003; Edwards, 1965), Landau expansion method (Keestra et al., 2003), (Nesarikar, 1995), etc., has been proposed to study the interfacial properties. They confirmed a time-dependent elastic recovery in an external macroscopic stress (T. and Molde-naers, 2002). The rheological behavior of a suspension of elastic and slightly deformable spheres in a Newtonian fluid was first treated by Froehlich and Sack in 1946 (Nesarikar, 1995), (Carreau et al., 1994). The elastic properties arising from interfacial tension effect in a dilute emulsion of two Newtonian fluids was modeled by Oldroyd (1950) (Bousmina, 1999). According to Oldroyd,

$$\eta_B = \eta_M \left[1 + \phi_D \frac{5K + 2}{2(K + 1)} + \phi_D^2 \frac{(5K + 2)^2}{10(K + 1)^2} \right] \quad (3.1)$$

Where η_B and η_M are the viscosities of the blend and matrix, while ϕ_D is the volume fraction of the dispersed phase, and K is a constant defined as

$$K = \frac{\eta_D}{\eta_M} \quad (3.2)$$

Kerner et al. (Bousmina, 1999), (Kerner, 1956) modeled the rheological behavior of a composite of two elastic bodies without interfacial tension even though the derivations were flawed, the final result showed good agreement for incompressible media. Table 3.2 shows a brief list of the various models proposed over the time.

Palierne et al. (1990, 1991) (Yu et al., 2002) proposed a general model to account for the viscoelastic behavior of phases, ignoring the steric interactions. According to Palierne (Yu et al., 2002), for an emulsion of two viscoelastic phases with uniform particle size and constant interfacial tension,

Table 3.2 List of various models proposed to measure the interfacial tension and their limitations (Bousmina, 1999).

	Model	Limitation
1. Wu et al. (2004), Song and Springer (1996)	Pendant drop model	High viscosity of polymer melt limits the application of this model
2. Elmendrop and de Vos (1986), Otsubo and Prud'homme (1994)	Spinning drop model	Longer time required to achieve equilibrium
3. Meijer et al. (1988) Van Puyvelde et al. (2001), Sundararaj and Macosko (1995)	Breaking drop model	

$$G_{B(\omega)}^* = G_{M(\omega)}^* + \frac{1 + 3\phi H_{(\omega)}}{1 - 2\phi H_{(\omega)}} \quad (3.3)$$

Here,

$$H = \frac{4\left(\frac{\alpha}{R}\right) \left[2G_{M(\omega)}^* + 5G_{D(\omega)}^* \right] + \left(G_{D(\omega)}^* - G_{M(\omega)}^* \right) \left(16G_{M(\omega)}^* + 19G_{D(\omega)}^* \right)}{40\left(\frac{\alpha}{R}\right) \left(G_{M(\omega)}^* + G_{D(\omega)}^* \right) + \left(2G_{D(\omega)}^* + 3G_{M(\omega)}^* \right) \left(16G_{M(\omega)}^* + 19G_{D(\omega)}^* \right)} \quad (3.4)$$

In the Palierne model, it is assumed that the dispersed phase exist as spheres and was found to be successful for molten polymer blends in the low frequency and high frequency regimes (Bousmina, 1999). Similarly, the dependence of interfacial tension (α) on local changes of interfacial area and the effect of local shear are virtually impossible to determine experimentally and are set to zero. By setting the interfacial tension (α) to zero, Palierne model becomes equal to the Kerner's model as (Bousmina, 1999)

$$G_B^* = G_M^* \frac{(2G_D^* + 3G_M^*) + 3\phi(G_D^* - G_M^*)}{2(G_D^* + 3G_M^*) - 2\phi(G_D^* - G_M^*)} \quad (3.5)$$

G_B^* , G_M^* , G_D^* are the dynamic modulus of the blend, matrix, and dispersed phase, respectively, α is the interfacial tension, and R is the volume of the dispersed phase. Table 3.3 shows the main advantages and limitations of the Palierne model.

Significant deviation of the experimental results from the Palierne model has been reported by Riemann et al (Riemann et al., 1997) (Riemann et al., 1996), Velankar et al (Martin and Velankar, 2007), Jacobs et al (Jacobs et al., 1999), etc. The Palierne model fails in the case of high impact polystyrene (HIPS) where “salami type” morphology is observed (Shi et al., 2006), (Horák et al., 2000). The model also fails in the case of blends with block

Table 3.3 List of main advantages and limitations of the Palierne model (Bousmina, 1999), (Tyagi et al., 2002).

Palierne model	Advantages	Limitations
	Viscoelasticity of both the phases, hydrodynamic interactions, droplet size and size distribution, interfacial tension, is included.	(1) Effect of gravity and inertia are neglected. (2) Limited to linear viscoelastic region. (3) Morphology changes during flow (break-up or coalescence) cannot be predicted. (4) A general behavior of the interface is considered.

copolymers (Shi et al., 2006). Graebing and Muller (1991) proposed a new model to study the interfacial properties of polymer melts (Graebing and Muller, 1991). Graebing et al. used Cole–Cole plots to follow the relaxation and zero shear viscosity of immiscible polymer blends systems using poly(styrene) (PS)–poly(methylmethacrylate) (PMMA) blends (Graebing and Muller, 1991). Later, Gramespacher et al. used the weighed relaxation time spectra ($\tau_{H(\tau)}$) to study the interfacial tension (Gramespacher and Meissner, 1992). This was based on the reports of Scholtz et al. (1989) (Gramespacher and Meissner, 1992) and Graebing et al. (1994) (Graebing and Muller, 1991).

Accordingly,

$$G_B^* = G_{M/D}^* + G_{\text{interface}}^* \quad (3.6)$$

This is based on the assumption that the complex modulus consists of two contributions: (1) the viscoelastic properties of the blend components and (2) the interfacial tension between the blend components. Thus, assuming a droplet-matrix type morphology,

$$= \phi G_M^* + (1 - \phi) G_D^* + G_{\text{interface}}^* \quad (3.7)$$

here ϕ is the volume fraction. Using the theory of mixture of Newtonian liquids developed by Choi and Schowalter (1975), (Choi and Schowalter, 1975) further modified by Scholtz et al. (1989) (Gramespacher and Meissner, 1992), the G' and G'' can be expressed as

$$G'_{(\omega)} = \eta \frac{\omega^2(\tau_1 - \tau_2)}{1 + \omega^2\tau_1^2} = \frac{\eta}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1} \right) \frac{\omega^2\tau_1^2}{1 + \omega^2\tau_1^2} \quad (3.8)$$

$$G''_{(\omega)} = \eta \frac{\omega^3\tau_1\tau_2 - \omega}{1 + \omega^2\tau_1^2} = \frac{\eta}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1} \right) \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + \omega\eta \frac{\tau_1}{\tau_2} \quad (3.9)$$

$$\eta = \eta_M \left[1 + \varphi \frac{5K+2}{2(K+1)} + \varphi^2 \frac{5(5K+2)^2}{8(K+1)^2} \right] \quad (3.10)$$

$$\tau_1 = \tau_0 \left[1 + \varphi \frac{5(19K+16)}{4(K+1)(2K+3)} \right] \quad (3.11)$$

$$\tau_2 = \tau_0 \left[1 + \varphi \frac{3(19K+16)}{4(K+1)(2K+3)} \right] \quad (3.12)$$

$$\tau_0 = \frac{\eta_M R}{\alpha} \frac{(19K+16)(2K+3)}{40(K+1)} \quad (3.13)$$

R is the radius of the dispersed droplets, and α is the interfacial tension. Thus,

$$G'_B = \varphi G'_M + (1-\varphi)G'_D + \frac{\eta_0}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1} \right) \left(\frac{\omega^2 \tau_1^2}{1 + \omega^2 \tau_1^2} \right) \quad (3.14)$$

and

$$G''_B = \varphi G''_M + (1-\varphi)G''_D + \frac{\eta_0}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1} \right) \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \quad (3.15)$$

The last term in the above Eqs. (3.14) and (3.15) describes the simple Maxwell model behavior where the spring modulus $(G) = \frac{\eta}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1} \right)$

To calculate the interfacial tension, the G' and G'' values are coupled to relaxation time spectrum as,

$$G'_{(\omega)} = \int_{-\infty}^{+\infty} H_{\tau} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d \ln \tau \quad (3.16)$$

$$G''_{(\omega)} = \int_{-\infty}^{+\infty} H_{(\tau)} \frac{\omega \tau}{1 + \omega^2 \tau^2} d \ln \tau \quad (3.17)$$

Thus, a plot of weighed relaxation spectrum $\tau H_{(\tau)}$ against $\log \tau$ can be used to calculate the interfacial tension (Gramespacher and Meissner, 1992). Doi and Ohta theory (1991) was used to develop a new model by Lee and Park (1994) (Lee and Park, 1994). General expression of stress tensor for an emulsion by Mellema and Willemsse (1983) was used as the base (Lee and Park, 1994).

$$\begin{aligned} \sigma_B = & \eta_B \dot{\gamma}_B + \lim_{v \rightarrow \infty} \frac{1}{V} (\eta_D - \eta_M) \\ & \times \int (u_M n_D - u_D n_M) ds + \lim_{v \rightarrow \infty} \frac{1}{V} \int a \left(\frac{1}{3} \nabla_B - n_M n_D \right) ds - P \nabla_B \end{aligned} \quad (3.18)$$

Here, $\dot{\gamma}$ is the sum of the components of rate of deformation tensor and velocity gradient tensor for the blend components, s is the area of the interface, ∇_B is the Kronecker delta function, and n is the vector normal to the interface.

$$q_B = \lim_{V \rightarrow \infty} \frac{1}{V} \int \left(n_B - \frac{1}{3} \nabla_B \right) ds \quad (3.19)$$

Here, q_B is the interfacial tensor as defined by [Onuki \(1987\)](#), second term on the right-hand side of (18) is called the viscosity ratio term and the third term is called the anisotropy tensor term ([Lee and Park, 1994](#)). Similarly,

$$\lim_{V \rightarrow \infty} \frac{1}{V} (\eta_D - \eta_M) \int (u_D n_M - u_M n_D) ds = \frac{6}{10} \left(\frac{\eta_D - \eta_M}{\eta_D + \eta_M} \right) \eta_M \phi \dot{\gamma} \quad (3.20)$$

Thereby, substituting (3.19) and (3.20) in (3.18) we get,

$$\sigma_B = \left(1 + \frac{\eta_D - \eta_M}{10(\eta_D + \eta_M)} \right) \eta_M \dot{\gamma} - a q_B - P \nabla_B \quad (3.21)$$

The important factors that determine the interface tensor includes (1) flow—as flow orients and enlarges the interface (2) interfacial tension that opposes the effect of flow. Thereby,

$$\frac{\partial q_B}{\partial t} = \left(\frac{\partial q_B}{\partial t} \right)_{\text{flow}} + \left(\frac{\partial q_B}{\partial t} \right)_{\text{interfacialtension}} \quad (3.22)$$

$$= K_B q_B - C_1 \frac{a}{\eta_M} Q^2 - C_3 \frac{a}{\eta_M} q_B \quad (3.23)$$

$$\left(\frac{\partial q_B}{\partial t} \right)_{\text{interfacialtension}} = -C_1 \frac{aQ}{\eta_M} \left(\frac{q_B}{Q} \right) \quad (3.24)$$

Here, C_1 , C_2 , and C_3 are dimensionless parameters which depend on the volume fraction of the dispersed phase. Thus, combining (3.23) and (3.24) yields

$$\left(\frac{\partial q_B}{\partial t} \right)_{\text{interfacialtension}} = -d_1 \frac{a}{\eta_M} Q q_B - d_1 d_3 \frac{a}{\eta_M} \left(\frac{q_B}{Q} \right) \quad (3.25)$$

$$\left(\frac{dQ}{dt} \right)_{\text{interfacialtension}} = -d_1 d_2 \frac{a}{\eta_M} Q^2 - d_1 d_3 \frac{a}{\eta_M} q_B \quad (3.26)$$

Here, $d_1 = C_1 + C_2$, $d_2 = C_1/(C_1 + C_2)$, and $d_3 = C_3/(C_1 + C_2)$ denotes the degree of total relaxation, size relaxation, break-up, and shape relaxation. Thus, by applying the Cox-Mertz rule, Lee and Park obtained the following ([Lee and Park, 1994](#)):

$$G_B^* = \left(1 + \frac{6(G_D^* - G_M^*)}{10(G_M^* + G_D^*)} \right) G_M^* + G_{\text{Interface}}^* \quad (3.27)$$

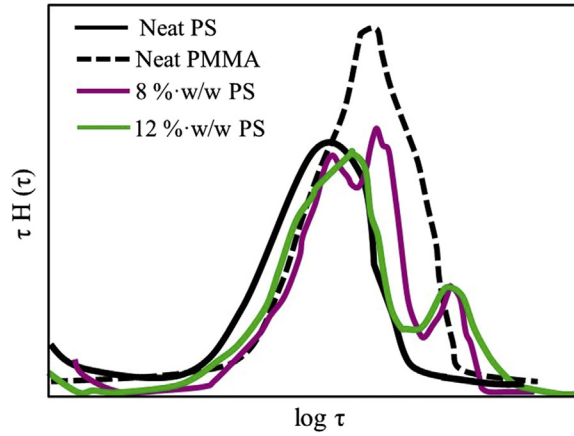
Bousmina (1999) derived a simple expression for the complex shear modulus by extending the Kerner model to viscoelastic media. This was then compared with the Palierne model and then applied to PS-PE blend system.

$$G_B^* = G_M^* \frac{2\left(G_D^* + \frac{\alpha}{R}\right) + 3G_M^* + 3\varphi\left(G_D^* + \frac{\alpha}{R} - G_M^*\right)}{2\left(G_D^* + \frac{\alpha}{R}\right) + 3G_M^* - 2\varphi\left(G_D^* + \frac{\alpha}{R} - G_M^*\right)} \quad (3.28)$$

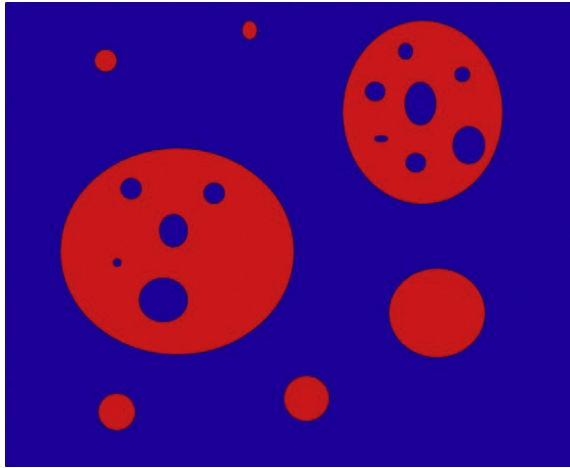
3. Application of the theories to various blend systems

Polystyrene (PS)–poly(methyl methacrylate) (PMMA) blend is one of the most thoroughly studied system. Han et al. reported the application of various models to study the interfacial tension and properties for PS-PMMA blends (Chuang and Han, 1984). According to Han et al. the blend can be considered as a weak viscoelastic liquid due to the presence of a weak plateau zone in the low frequency zone (Chuang and Han, 1984). Similarly two relaxations, one at low frequency corresponding to PMMA and another at high frequency corresponding to that of PS were reported (Chuang and Han, 1984). Graebing et al. proposed the use of Cole–Cole plots to study the relaxations and zero shear viscosity for three different blend systems of poly(dimethyl siloxane) (PDMS)–poly(oxyethylene) (POE-DO), PS-PMMA, and PS-poly(ethyl methacrylate) (PEMA) (Graebing and Muller, 1991), (Graebing et al., 1994). Graebing et al. coined that the main weakness of the interfacial tension calculation using viscoelasticity measurement is the error in particle size measurement, considering the fact that the precise determination of blend morphology is often very difficult (Graebing and Muller, 1991). Gramespacher et al. reported the weighed time relaxation spectra for PS-PMMA blend system and used it to study the interfacial properties (Gramespacher and Meissner, 1992). PS-PMMA blends were prepared using twin screw extruder at 200 °C. PS having M_n of 11,000 g mol⁻¹, M_w of 31,400 g mol⁻¹ and PMMA with M_n of 47,000 g mol⁻¹ and M_w of 83,000 g mol⁻¹ were used for the study. Fig. 3.2 shows the weighed time relaxation spectra for PS-PMMA blend system.

They concluded that an additional Maxwell element with a characteristic relaxation time can be used to calculate/explain the influence of interfacial tension between two immiscible polymer blends. This can also be used to characterize the compatibilizer efficiency. A limitation of the method is that it can be applied only when the blend components have similar temperature dependence of zero shear viscosities. Riemann et al. (1994) reported a phase in phase (or sphere in sphere) (sis) morphology for PS-PMMA blends (Riemann et al., 1994). A detailed investigation of the interfacial properties and morphology of PS-PMMA blends with sis morphology was reported by (Fahrländer and Friedrich, 1999). PS-PMMA blends with PS as matrix and PMMA (between 10% and 30% w/w) as dispersed spheres were prepared by dissolving in THF followed by precipitation using methanol (Fig. 3.3).

**FIGURE 3.2**

Weighed time relaxation spectra for (A) neat PS, (B) blend with 8% w/w of PS, and (C) blend with 12% w/w of PS (Gramespacher and Meissner, 1992).

**FIGURE 3.3**

Shows a schematic representation of the phase in phase (sphere in sphere) (sis) morphology for PS-PMMA blends with PS as the matrix (Fahrländer and Friedrich, 1999).

To account for the sis morphology, Palierne model was modified as (Fahrländer and Friedrich, 1999)

$$G_B^* = G_M^* \frac{1 + 3(\varphi_2 H_{2(\omega)} + \varphi_3 H_{3(\omega)})}{1 - 2(\varphi_2 H_{2(\omega)} + \varphi_3 H_{3(\omega)})} \quad (3.29)$$

Where,

$$H_{2(\omega)} = \frac{4 \frac{\alpha}{R_2} (2G_{M(\omega)}^* + 5G_{C(\omega)}^*) + (G_{C(\omega)}^* - G_{M(\omega)}^*) (16G_{M(\omega)}^* + 19G_{C(\omega)}^*)}{40 \frac{\alpha}{R_2} (G_{M(\omega)}^* + G_{C(\omega)}^*) + (2G_{C(\omega)}^* + 3G_{M(\omega)}^*) (16G_{M(\omega)}^* + 19G_{C(\omega)}^*)} \quad (3.30)$$

and

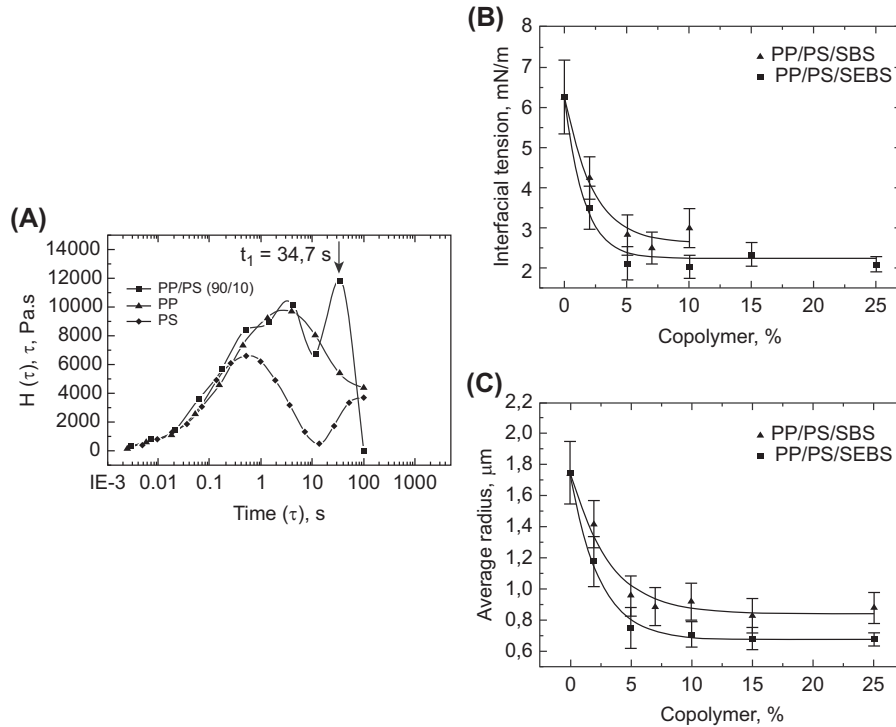
$$H_{3(\omega)} = \frac{4 \frac{\alpha}{R_3} (2G_{M(\omega)}^* + 5G_{D(\omega)}^*) + (G_{D(\omega)}^* - G_{M(\omega)}^*) (16G_{M(\omega)}^* + 19G_{D(\omega)}^*)}{40 \frac{\alpha}{R_3} (G_{M(\omega)}^* + G_{D(\omega)}^*) + (2G_{D(\omega)}^* + 3G_{M(\omega)}^*) (16G_{M(\omega)}^* + 19G_{D(\omega)}^*)} \quad (3.31)$$

$G_{M(\omega)}^*$, $G_{D(\omega)}^*$, $G_{C(\omega)}^*$ are the complex modulus of the matrix (PS), dispersed phase (PMMA), and composite (sis) or particles with phase in phase morphology, respectively (Fahrländer and Friedrich, 1999). The experimental results were fitted with the Palierne model and modified Palierne model, and they concluded that in the case of blends with sis morphology the modified Palierne model showed a better agreement with the experimental results. Similarly, the relaxation of particle with sis morphology occurs in the experimentally accessible frequency range and they have decisive role in the behavior of the blends. Marcaubus and Demarquette (1999) investigated the morphology and interfacial properties of PS-PP blend system compatibilized with styrene-butadiene-styrene (SBS) or polystyrene–poly(ethylene-*co*-butylene)—polystyrene (SEBS) block copolymers. Table 3.4 shows the characteristics of PP and PS used for the study. (Macaúbas and Demarquette, 1999).

About 2–25%•w/w of compatibilizer was first added to PS (which form the minor phase) followed by the addition of PP in a twin screw extruder at 200°C. PP-PS blend system 10%•w/w of PS was used for the study. The blends showed an increase in elasticity at low frequencies which can be related to the relaxation of the droplets that form the dispersed phase. The blends were not showing a secondary plateau making the use of Graebing model to calculate interfacial tension difficult. The interfacial tension calculated using the Gramespacher and Meissner model showed good agreement with experimental results (Macaúbas and Demarquette, 1999), (Salehiyan et al., 2015) (Fig. 3.4).

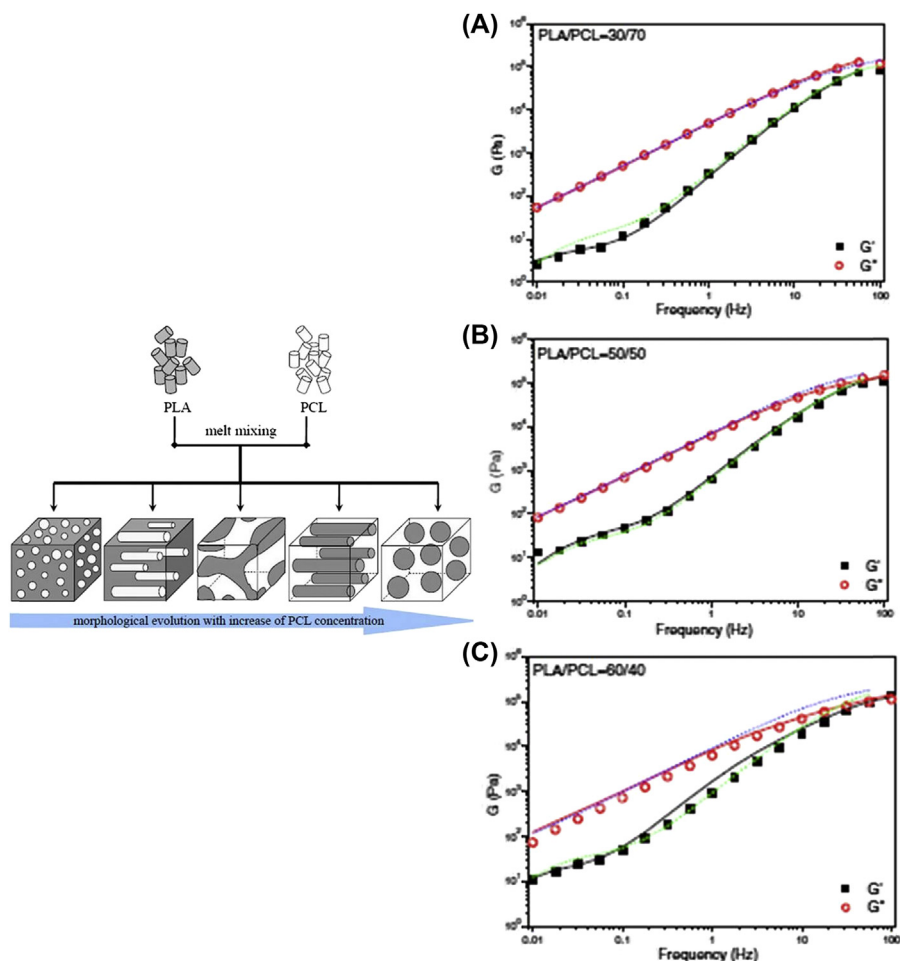
Table 3.4 Physical properties of PP, PS, and compatibilizer used for the study (Macaúbas and Demarquette, 1999).

Polymer	M_w (g•mol ⁻¹)	Melt flow index (MFI) (g•10min ⁻¹)	Compatibilizer (block copolymer)	
			Kraton D	Kraton G
PP	5.105	15	Linear SBS	Linear SE-BS
PS	228.1	22		

**FIGURE 3.4**

(A) Weighted relaxation time spectra for PP, PS, and blend system, (B) follows the interfacial tension as a function of the amount of compatibilizer, and (C) portrays the average radius of dispersed phase (PS) as a function of the compatibilizer concentration (Macaúbas and Demarquette, 1999).

Huo et al. studied the effect of compatibilization for PP-PS blend system using *in situ* compatibilization technique (Huo et al., 2007). Maleic anhydride grafted PP and amine terminated PS were used as compatibilizer to form a graft copolymers. In *in situ* compatibilized blends, the functional groups on polymer/precursor react with the components of the blend to form a copolymer at the interface (Huo et al., 2007). This has been widely applied for blends based on polyamide (Shi et al., 2006). Blends of poly(lactide) (PLA)—poly(ϵ -caprolactone) (PCL) have been widely studied due to their physical properties, biodegradability, and application in tissue engineering (Wu et al., 2008). Wu et al. (2008) reported the morphology and linear and nonlinear viscoelastic properties of PL-PCL blends. The experimental results obtained were treated with various models like Palierne model, Gramespacher and Meissner model (Wu et al., 2008). Fig. 3.5 shows the schematic representation of various morphologies that can be obtained while mixing PLA and PCL along with the experimental results and their fitting with various models (Wu et al., 2008).

**FIGURE 3.5**

Schematic representation of the various types of morphologies that can be expected while mixing PLA with PCL, G' and G'' plots for (A) 30–70 blend, (B) for 50–50 blends, and (C) for 60–40 blends along with the fitting with Palierne model, Gramespacher and Meissner model (Wu et al., 2008).

They concluded that the phase inversion occurs at 60% w/w of PLA. Similarly the Palierne model showed a better fit to the linear viscoelastic properties of blend when compared with the Gramespacher and Meissner model, although both the theories fail in the case of blend with co-continuous structure (Wu et al., 2008). Yu et al. (2007) studied the relaxation behavior of thermoplastic liquid crystalline polymer (TLCP) using optical microscopy and rheology. TLCP (a copolymer of 80% *p*-hydroxybenzoic acid and 20% poly(ethylene terephthalate)) was analyzed using Haake Rheostress 300 with parallel plate of 20 mm diameter and gap 1 mm. They concluded that the solid

crystals greatly influence the relaxation behavior (Yu et al., 2007). The solid particles impose constraints on the relaxation of chains and polymer domains so that the time of relaxation for chain orientation and deformed poly domains are longer at lower temperatures than at higher temperatures. Thus, at longer relaxation times, the domain coalescence predominates (Yu et al., 2007). Phase behavior and actuating morphology of polybutadiene (PB)–low vinyl content polyisoprene (PIP) blend system was investigated in detail by Zou et al. (Zou et al., 2014). PB having M_n of 44,000 g mol⁻¹, PDI of 1.03, and density of 0.895 g cm⁻³ was mixed with low vinyl content polyisoprene having M_n of 66,000 g mol⁻¹, PDI of 1.04, and density of 0.897 g cm⁻³. The blends were prepared by solution casting technique. The terminal relaxation behavior of PIP and PB was confirmed by following the $G'\alpha\omega^2$ and $G''\alpha\omega$ behaviors (Zou et al., 2014). They concluded that power law behavior of the dynamic storage modulus at low angular frequency is observed for near critical and symmetric blends with co-continuous phase separating structure. Similarly the droplet size and characteristic relaxation time calculated from rheology showed excellent correlation with the droplet dimensions calculated by SALS and rheology. Symmetric and near critical blend compositions obeyed the power law behavior at low angular frequencies. For off-critical and asymmetric blends, the simplified Palierne model successfully explained the complex elastic behavior at mediate and low angular frequencies (Zou et al., 2014).

Dean Shi et al. reported the relaxation behavior of compatibilized and uncompatibilized blends of PP-polyamide-6 (PA6), with maleic anhydride grafted PP (MA-g-PP) (with 1.03% of maleic anhydride content) being used as the compatibilizer (Shi et al., 2006). Details of the materials used are shown in Table 3.5.

Palierne model successfully explained the experimental results for low amounts of the dispersed phase (to 10%·w/w), while it failed for higher amounts of the dispersed phase (30%·w/w) and for compatibilized blend systems. The form relaxation time defined as the time required for the deformed spheres to regain their original spherical shape can be predicted from the Palierne emulsion model as

$$\tau_1 = \frac{R_v \eta_M}{4\alpha} \left(\frac{(19K + 16)(2K + 3 - 2\phi_D(K - 1))}{10(K + 1) - 2\phi_D(5K + 2)} \right) \quad (3.32)$$

Table 3.5 Details of the materials used by Dean Shi et al. for study (Shi et al., 2006).

Materials	Mw (kg·mol ⁻¹)	Mn (kg·mol ⁻¹)	ρ (25°C) (g·cm ⁻³)	η_o (at 230°C) (Pa·s)	τ_o (230°C) (s)
PP	259	65	0.902	1300	0.35
PA6	–	24	1.14	1250	0.03
PP-g-MAH	320	59	0.902	50	0.25

Table 3.6 Experimental and theoretical relaxation times for PP-PA6 blends and blends compatibilized with PP-*g*-MAH (Shi et al., 2006).

PP-PP- <i>g</i> -MAH-PA6 (by mass)	τ (s) (experimental)	τ (s) (theoretical)	
		Without interfacial relaxation	With interfacial relaxation
90-0-10	1.1	1.1	— ^a
70-0-30	17.3	5.9	— ^a
45-45-10	26	0.1	21.1
35-35-30	17	0.1	36.5
80-10-10	40	0.2	37.1
60-10-30	42	0.5	84.1

^a In the case of uncompatibilized blends, no form relaxation was observed as it becomes merged with the matrix relaxation.

Considering the interfacial relaxation, the form relaxation time becomes

$$\tau_{\beta} = \frac{t_1}{2} \left(1 + \left(1 - 4 \frac{t_1}{t_2} \right)^{1/2} \right) \quad (3.33)$$

Table 3.6 shows the experimental and theoretical relaxation times as calculated by Dean Shi et al. (Shi et al., 2006).

The large deviation in theoretical and experimental relaxation times observed for blends with high amount of dispersed phase, compatibilized blends was explained by the unique morphologies encountered in transmission electron microscopy studies. The effect of nanoclay in stabilizing and controlling the morphology of PP-PA6 ternary nanocomposites was reported by Huang et al. (Huang et al., 2014).

4. Conclusion

The significance of studying interfaces in polymer blends is investigated in detail. The morphology and ultimate properties of the blend depend on (1) rheological properties of the phases, (2) blend composition, (3) processing conditions, and (4) interfacial tension. Various theories and models proposed over the time like Palierne model, Graebling and Miller model, and Gramespacher and Meissner model have their own advantages and limitations. PS-PMMA blend is one of the thoroughly investigated systems over the years especially due to the different types of morphologies that can be produced by using different mixing techniques. Standing within the concentration limits, PS-PMMA blends show two different types of morphology depending on the method of blend preparation. Melt mixing gives a usual morphology of PMMA droplets dispersed in PS matrix, while solution cast blends show a phase in phase or sphere in sphere (sis) morphology. Vanoene (1972) dealt with this problem considering the fact that under conditions of flow, the more elastic

component which forms the matrix tends to lower the effective interfacial tension. A particular problem of significant importance is the error in determining dispersed phase particle size which limits the application of various models discussed above. Experimental results of usual droplet matrix morphologies can be modeled with the simple Palierne equation. In the case of PP-PS blend system, Gramespacher and Meissner model showed good agreement with the experimental results. In the case of blends with unusual morphologies, like sis morphology or the salami type morphology (observed for HIPS), the Palierne model need to be modified. Thus, the aim of generating a universal model applicable to all types of morphologies encountered is still being pursued.

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Rheology of colloidal particle suspensions

4

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Abstract

This article summarizes the series of different methodologies to evaluate rheology of colloidal particle suspensions and different approaches to correlate this macroscopic behavior with microscopic particle–particle interaction. This includes the coupling suspension yield stress and Derjaguin–Landau–Verwey–Overbeek forces, i.e., van der Waals and electrical double layer forces. This summary provides a better understanding of the basic phenomena associated, historical development, and current status of colloidal suspension rheology and also discusses its applicability and limitations/variations to different types of concentrated particle suspensions. Aqueous suspensions discussed are composed of colloidal particles, including polymers, and their nanocomposites with metal oxide/clay particles. The research gaps are identified and specific future perspectives are discussed to further enhance the use of suspension rheology and to aim for the transition from the evaluation of simple particle suspension systems to more complex particle suspension systems that fit more with the current and future industry needs in particle processing.

Keywords: Complex particle system; Concentrated suspension; DLVO forces; Geometry; Measurement; Particle–particle interaction; Zeta potential.

1. Introduction

Our daily products and industrial products are often made of colloidal size particles (e.g., 10 nm–1 μ m) either produced by top-down methods (i.e., crushing and grinding to produce fine powders) or formulated by bottom-up methods (i.e., synthesis of colloidal size particles). Such colloidal products can be particle dispersion (e.g., starch aqueous solution), emulsions (e.g., oil-in-water emulsions, such as ice cream, milk; water-in-oil emulsions, such as mayonnaise, margarine, and butter), foams (e.g., egg white foam), oil droplets, and proteins. Fig. 4.1 shows those typical categories of food colloid dispersions/suspensions. In addition, Table 4.1 shows the list of keywords appeared in food colloid conferences organized by the Royal Society of Chemistry.

Table 4.1 shows the list of different food colloids together with their physical properties (e.g., size ranges, sphericity/nonsphericity (general, unique)), applications,

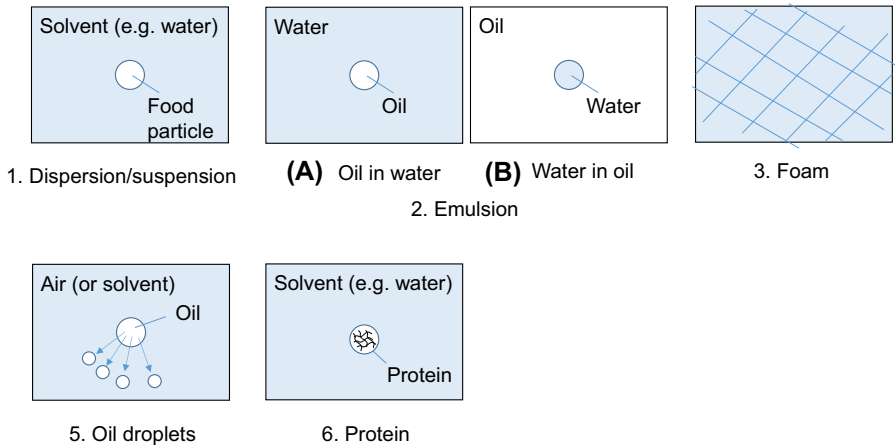


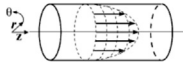
FIGURE 4.1

Typical categories of food colloid dispersions/suspensions.

Table 4.1 Keywords appeared in 11 edited proceedings of European food colloid conferences (1986–2006) published by the Royal Society of Chemistry (Dickinson, 2011).

Keyword	Number
Protein(s)	108
Emulsion(s)	79
Interface(s)/interfacial	59
(Micro)structure(s)/structural	53
Gel(s)	43
Adsorbed/adsorption	35
Interaction(s)	33
Stability	31
Casein(ate)	28
Foam(s)	28
Rheology	22
Surfactant(s)	21
Particle(s)	20
Polysaccharide(s)	17
β-Lactoglobulin	17
Aggregation	16
Others	≤15

Table 4.2 Different type of flows and rheological measurement geometries.

Type of flow	Geometry (Boger, 2009)	Potential application
Poiseuille flow		Pipeline
Couette flow		Stirring tank
Parallel plate torsion		Pasting
Cone and plate torsion		Pasting

unique behaviors once formulated in concentrated dispersions/suspensions (e.g., shear thickening of starch), pH in water, and non-aqueous medium required to disperse.

They give us some insight about the commonalities between general colloid and interface science and food colloids, regarding types of colloids dealt with and the areas of studies and issues. Understanding microscopic particle–particle interactions and macroscopic behaviors of different colloid suspensions can be performed with the application of theories and characterization methods developed for conventional colloids and interface science.

For example, one of the most important characteristics we need to know to formulate concentrated colloids is their stability that can be explained in several different ways.

Stability in terms of dispersion/coagulation in a colloidal suspension can be evaluated by using the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory. The evaluation of colloidal stability and instability will be further explained in the following section in detail.

Difficulties and challenges associated with handling and formulating concentrated colloid dispersions/suspensions in a suspending medium and reported issues in the past are summarized in this chapter.

Particle aggregation leads the particle sedimentation, and thus with time particle–liquid separation that is against the aim of formulating a stable colloid dispersion/suspension. Its long life stability is one of the major challenges remained unsolved. Thus, a good colloidal particle dispersion together with long stability is a well-deserved property of those colloid dispersions/suspensions.

In addition, in multi-component systems, the competitive adsorption of surfactants and/or polymer may happen. In food emulsions, for example, a mixture of polymer species as well as low-molecular weight surfactant may be present

(Dickinson and Euston, 1992). Thus, understanding those adsorptions can be significantly important to formulate the stable food colloids/emulsions (Dickinson and Euston, 1992).

Particle–particle interaction determines a food colloidal suspension texture as well as its macroscopic behavior, such as thickening and thinning under a certain shear loading. Thus, understanding the microscopic interactions and its correlation with macroscopic behavior is crucial part of colloid characterization and formulation.

Instability issues have been reported for different types of colloidal suspensions/dispersions [e.g., (Raikos, 2010)]. Milk, for example, can be unstable with the application of the heat or changing chemical environment. As an example, coffee together with soy milk can be forming weak aggregates, whereas coffee together with cow milk produces a good stable dispersion (Fig. 4.2). This difference can be explained by the difference in the surface charge of protein particles in different milks. Fig. 4.3 shows the zeta potential of those two milk proteins as a function of pH, (A) cow milk

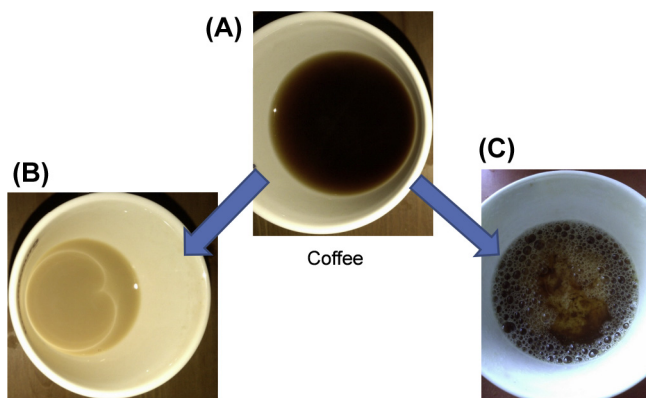


FIGURE 4.2

Pictures of (A) coffee, (B) coffee with cow milk, and (C) coffee with soy milk.

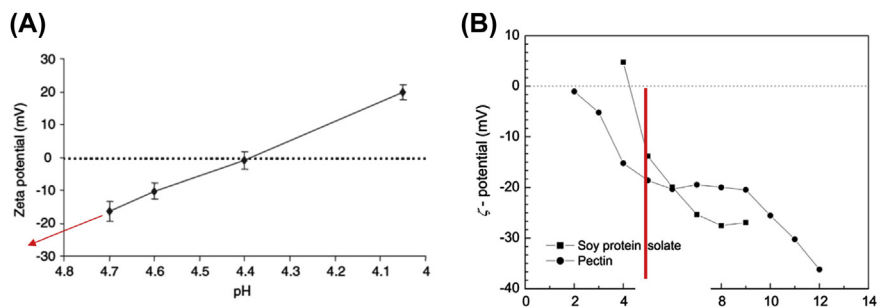


FIGURE 4.3

Zeta potential of (A) milk protein (Sejersen et al., 2007) and (B) soy protein isolate and pomelo pectin (Krongsin et al., 2015), as a function of pH.

and (B) soy milk. The pH of a coffee solution is around pH 5–5.1 (Rothstein, 2017) that gives the zeta potential of cow milk and soy milk around -30 mV (Sejersen et al., 2007) and -15 mV (Krongsin et al., 2015), respectively. Considering the small magnification of zeta potential of proteins in soy milk around the pH of coffee, it can lead to their aggregation due to the stronger influence of the van der Waals force, while cow milk proteins disperse/repel each other at that pH due to the stronger influence of the electric double layer force.

In colloidal particle processing, including food processing as an example, a proper dispersion/disaggregation of colloidal particles in a concentrated aqueous suspension plays a significantly important role in achieving good handling and manipulation of those colloidal suspensions [e.g., (Otsuki and Bryant, 2015)]. In this chapter, concentrated colloidal particle dispersions/suspensions with the particle size range in the order of single nanometers to around 10 micron meter is of our major concern that can be recognized as nanostructures formed by crystal structures as well as microstructures that determine the macroscopic suspension behaviors. Within that size range, submicron to 10 micron meter is directly relevant to the current and long-standing issues in their processing [e.g., (Crawford and Ralston, 1988)] and characterization [e.g., (Otsuki and Bryant, 2015)]. Currently, many methods are available for characterizing colloidal particles by measuring size [e.g., (Nguyen et al., 2006a)], turbidity [e.g., (Askarieh et al., 2010)], zeta potential [e.g., (Mitchell et al., 2005)], and the combination of these methods [e.g., (Yoon et al., 1997; Yates et al., 2005)]. On the other hand, these methods often require a dilute suspension [e.g., (Kralchevsky et al., 2008)] and could overlook the coagulation potentially occurring and depressing the process efficiency in concentrated suspensions that are commonly treated in many different plant operations [e.g., (Otsuki and Bryant, 2015)]. Such coagulation can be caused by an increase in particle–particle interactions as suspension concentration increases. Those coagulations have been reported by many researchers [e.g., (Hunter and Nicol, 1968; Russel et al., 1989)]. Otsuki et al. (2011) also reported the effects of higher solid concentrations and mixing two different types of particles on the shear yield stress, a good indicator of the particle interactions that determine their coagulation/dispersion. Significantly higher yield stress/particle interactions were reported in a concentrated mixed coagulating particle system (i.e., 2.5 Pa in 5 vol.%, 28 Pa in a 10 vol.% nickel oxide–hematite particle mixture) than in a single particle system with a lower particle concentration (i.e., 0.5 Pa in 5 vol.%, 4.5 Pa in 10 vol.% nickel oxide). Their cases indicated the heterocoagulation of their dissimilar particles more pronounced due to the stronger particle interactions in a higher solid concentration and alkaline pH, and thus increased the suspension yield stress (Otsuki et al., 2011).

Complex particle systems, including complex food colloid dispersions/suspensions, are of great interest of industrial processes everywhere. For example, new formulations of foods consist of many different ingredients to provide desired nutrients and have been a general trend of food industry [e.g., (Yaghmur et al., 2004)]. This trend creates a challenge associated with proper characterization of those newly formulated foods, especially in the concentrated dispersions/suspensions because

there can be higher particle–particle interactions and thus particle aggregation that must be normally avoided to provide desired functions from each food component.

In addition, many process industries, including food industry, now hold a growing interest in increasing the solid concentration to achieve the higher process performance with less water consumption. Hence, the precise characterization and manipulation of particle dispersion and coagulation in a concentrated suspension/dispersion are strong assets to achieve such success in many industrial processes (Otsuki and Bryant, 2015; Franks, 2005). This article will introduce mainly two potential pathways to properly analyze and address the above issues by providing the basic phenomena associated. That includes the series of methodological and modeling development made to couple the DLVO forces and the suspension rheology to characterize and understand the particle–particle interactions in a concentrated colloid suspension/dispersion, and thus to provide useful information about the behavior of that particle suspension.

Suspension rheology reflects microscopic interactions between particles within a suspension/dispersion and detects the change in macroscopic behavior, such as an increase in the viscosity and/or yield stress due to the stronger particle interactions. Change in the viscosity can affect the process ability of a particle suspension/dispersion and thus process performance. The lower the viscosity by diluting a suspension, the higher the transportability; but less amount of particles can be processed. On the other hand, increasing the particle concentration would increase particle–particle interactions and the viscosity and thus lower the transportability and could result in the less process yield. In addition, so-called rheology modifiers can be used to maintain a reasonable process yield in many industrial applications, including mining and paintings [e.g., (Chana et al., 2007)]. Apparently, many companies dealing with particle suspension/dispersion systems are interested in increasing the particle/solid concentration to aim for a higher productivity as well as the effective waste/tailing management (Boger, 2009). Understanding the suspension rheology is one of the key tasks for someone who deals with concentrated colloidal particle suspensions/dispersions, to properly maintain and manipulate the process ability and thus achieve a good yield of his/her products through a proper suspension/dispersion processing.

This chapter introduces mainly shear suspension rheology. Among that category of rheology, the shear yield stress as a particle suspension property which can be determined by a rheological measurement. It is the minimum applied stress that must exceed to make a viscoplastic material flow like a liquid (Hackley and Ferraris, 2001). It reflects the structure formed and physical/chemical properties of the components, e.g., particle and liquid. Hydrodynamic force also called Stokes drag force ($F_h = 6\pi\mu_m aV$ where μ_m is the viscosity of the medium, a is the particle radius, and V is the velocity) (Mewis and Wagner, 2012) could affect the suspension rheology. It can influence the suspension yield stress with coarse particle suspensions more than colloidal particle suspensions. For example, in the case of 1 μm particle suspension in water sheared at low shear rate, it is negligible (2×10^{-15} N) (Mewis and Wagner, 2012). On the other hand, for colloidal particles, the particle–particle interactions

can significantly contribute to the change in the yield stress of suspension. Determination of the yield stress can be performed through mainly either of the following two different methods: (1) with a bob-in-cup geometry to measure and plot the shear stress as a function of shear rates and fitting the curve to extrapolate via the stress axis or (2) with a vane geometry to measure the shear stress at a low shear rate for a certain time period and determine the maximum stress as the yield stress [e.g., (Boger, 2009; Dzuy and Boger, 1983a)].

This chapter introduces the theory of colloidal particle dispersion/aggregation as well as stability/instability and then discusses the characterization methods focusing on suspension rheology experiments together with the application of DLVO theory to explain the particle–particle interaction as well as macroscopic suspension behaviors.

Thus, the specific aims of this chapter are as follows:

- To review the basic theory and phenomena involved, historical development, and current status of the characterization methods of concentrated colloid dispersions/suspensions;
- To review the applicability and limitation of different methods to evaluate the particle–particle interactions in a concentrated colloidal dispersion/suspension;
- To focus on reviewing the previous works on the rheological measurements of colloidal dispersions/suspensions to summarize the state-of-arts as well as the research gaps; and
- To provide the detail future perspectives one can take over to enhance our understanding and characterization of the concentrated colloidal dispersion/suspension and improve their formulation and manipulation.

Within the above frameworks, DLVO theory will be first revisited, followed by the review of application of suspension rheology measurements to characterize colloid dispersions/suspensions in terms of historical advancement and recent development toward the discussion on characterization of more complex food colloid systems, including multiingredient colloidal particle systems. The details of each component will be explained more in the following sections. Other relevant topics, such as the yield stress determination and coupling other physicochemical properties (e.g., zeta potential) with the DLVO forces, are out of the focus of this chapter. Some insights for such topics can be found in the chapters written by Nguyen et al. (2006b) and Otsuki (2018), respectively.

2. DLVO theory and its application to evaluate colloid systems

DLVO theory is a well-known theory for describing the particle–particle interactions with the summation of the van der Waals potential (V_{VDW}) and electrical double layer potential (V_{EDL}) (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). If the total potential energy ($V_T = V_{VDW} + V_{EDL}$) is high and positive

(commonly >15 kT), particles repel each other. On the other hand, if the total potential is negative, or a small positive value, particles attract each other. This is a straightforward theory which can explain particle coagulation/dispersion in many different colloidal systems [e.g., (Adamczyk and Weroni, 1999; Diao et al., 2014; Change et al., 2009)].

$$V_{VDW} = -\frac{Aa}{12H} \quad (4.1)$$

$$V_{EDL} = \frac{\epsilon a \zeta^2 \ln[1 + \exp(-\kappa H)]}{2} \quad (4.2)$$

$$\kappa = \left(\frac{2z^2 n_0 e^2}{\epsilon_0 \epsilon k T} \right)^{1/2} \quad (4.3)$$

where A_H is the Hamaker constant, H is interparticle separation distance, ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of free space, ζ is the zeta potential, κ is the Debye-Huckel reciprocal length defined in Eq. (4.3) where n_0 is the number concentration of ions, z is the ionic valence, e is the elementary charge, and T is the absolute temperature, k is the Boltzmann constant.

The van der Waals force is short range but accumulative and universal in any colloidal suspension/dispersion systems (Otsuki, 2018). The origin of this force is the instantaneous dipole interactions within atoms/molecules in neighboring particles. The nature of this interaction is attractive due to the correlation between dipoles to minimize their interaction energy (Israelachvili, 2011). The van der Waals force is normally independent on suspension conditions such as pH and presence of surfactant/polymer, except particle size and high electrolyte concentration (Johnson et al., 2000).

The electrical double layer force is the result of ion concentration between neighboring particle surfaces due to overlapping the double layer formed around the particle surface and thus increase in osmotic pressure and free energy (Israelachvili, 2011). Suspension pH can vary the zeta potential and thus the electrical double layer force. This force is repulsive in a similar particle system, while it can be either repulsive or attractive in a dissimilar particle system depending on the sign and magnitude of particle surface charges.

For two similar particles of radius a separated by distance H , where $a \gg H$, the van der Waals force (F_{VDW}) (Israelachvili, 2011) and the electrical double layer force (F_{EDL}) (Hogg et al., 1966) can be written as Eqs. (4.4) and (4.5), respectively:

$$F_{VDW} = -\frac{A_H}{12H^2} \quad (4.4)$$

$$F_{EDL} = \frac{2\pi\epsilon_0\epsilon\kappa\zeta^2 \exp(-\kappa H)}{1 + \exp(-\kappa H)} \quad (4.5)$$

Eqs. (4.4) and (4.5) are the major equations used in the coupling DLVO forces and suspension yield stress [e.g., (Ong and Leong, 2012; Leong and Ong, 2003; Flatt and Bowen, 2006)]. The equations for other systems can be found elsewhere [e.g., (Israelachvili, 2011)].

In addition to the conventional DLVO forces, one can also take into account other forces, including the steric forces that can be originated by the polymer adsorption onto the particles/droplets.

Methodologies of colloidal particle stabilization can be categorized into (Dickinson, 2003a)

1. Charge stabilization;
2. Polymer/steric;
3. External force application (e.g., mechanical, electrical).

Fig. 4.4 represents those three different types of particle stabilization in the use of polymers.

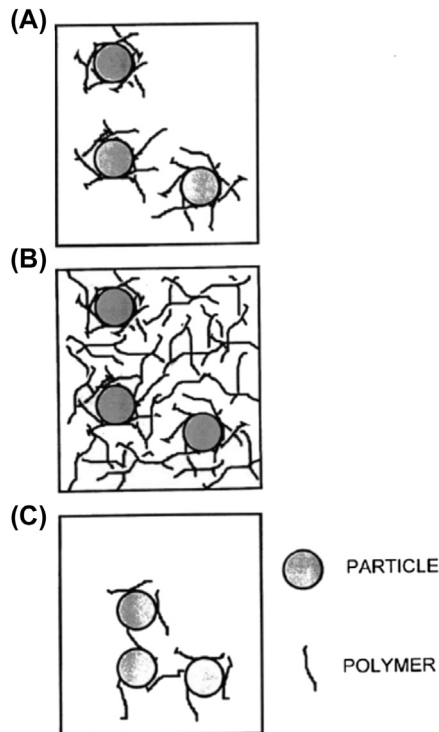


FIGURE 4.4

Effects of the polymer adsorption on the stabilization of spherical emulsion droplet (Dickinson, 2003a).

The long-term stability of food colloid dispersions/suspensions is one of their most important properties as well as challenges, and it should be properly characterized and applied to formulate the products with desired functions and nutrients.

The stability ratios [e.g., (Kobayashi et al., 2005)] can be defined as

$$W = k_{\text{fast}}/k \quad (4.6)$$

where k_{fast} is the fast aggregation rate for KCl concentration above 1 mol/L and the pH in the range of 6–11. The aggregate rate constant k of two spherical colloidal particles can be calculated by solving the steady-state diffusion equation (Kobayashi et al., 2005):

$$k = \frac{8}{3\beta\eta} \left\{ 2r \int_0^\infty \frac{B(h)}{(2r+h)^2} \exp[\beta V(h)] dh \right\}^{-1} \quad (4.7)$$

where η is the viscosity of the solution, h is the distance between particle surfaces, $B(h)$ is the hydrodynamic resistance function defined in Eq. (4.8), and $V(h)$ is the total potential energy defined by the DLVO theory (Kobayashi et al., 2005).

$$B(h) = \frac{6\left(\frac{h}{r}\right)^2 + 13\left(\frac{h}{r}\right) + 2}{6\left(\frac{h}{r}\right)^2 + 4\left(\frac{h}{r}\right)} \quad (4.8)$$

Fig. 4.5 shows the stability ratio as a function of electrolyte type and concentration. The intersect between the curve and $W = 1$ ($\log W = 0$) indicate the critical coagulation concentration (CCC), while below that threshold W the fast coagulation happens due to the stronger contribution of the van der Waals attraction (Tadros, 2007).

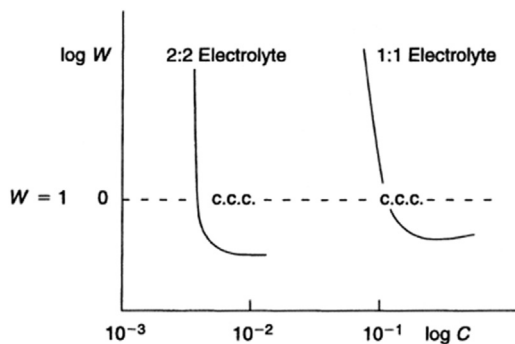


FIGURE 4.5

Stabilization ratio (W) as a function of concentration of 1:1 and 2:2 electrolytes.

This chapter will not provide the detail introductions to each category. Instead, specific example of food colloid stabilization will be introduced, i.e. the stabilization of emulsion that can be achieved by the steric stabilization and/or the electrostatic stabilization (Dickinson and Euston, 1992; Dickinson et al., 1988a; Dickinson et al., 1988b). To effectively stabilize dispersed colloidal particles or emulsion, the four criteria must be agreed (Dickinson, 2003b):

- (i) Strong adsorption;
- (ii) Complete surface coverage;
- (iii) Formation of a thick steric stabilizing layer; and
- (iv) Formation of a charged stabilizing layer.

A homopolymer cannot meet all the four criteria, while a block copolymer, composed of a small fraction of strongly adsorbing hydrophobic segments and the other large fraction of non-adsorbing hydrophilic segments does (Dickinson, 2003b). In addition to the above criteria, the high solubility of the stabilizing chain in the medium and strong solvation by its molecules was also mentioned. In other words, the Flory–Huggins interaction parameter x should be smaller than $1/2$ (Tadros and Tadros, 2007).

A potential cause of instability, for example, in a food oil-in-emulsion, is depletion flocculation by the presence of a small amount of water-soluble polymer (Dickinson, 2015), non-absorbing entities of surfactant micelles (Dickinson, 2015) or casein colloidal particles (Dickinson, 2015). The depletion contribution to the droplet pair interaction can be described by the Asakura–Oosawa depletion potential for the ideal case of two large spheres of radius R in a fluid of small spheres of diameter d_s as follows (Dickinson, 2015):

$$u_{dep}(d) = - \left(\frac{3kTR\phi_s}{d_s} \right) (d_s - d), \quad (d < d_s) \quad (4.9)$$

where ϕ_s is the volume fraction of the small spheres.

As indicated in this equation, an increase in ϕ_s and/or d_s-d provides the more negative potential leading the higher probability of large particle aggregation.

3. Rheology of colloidal systems

Suspension rheology reflects the microscopic interaction between particles within a suspension/dispersion and shows the change in macroscopic behavior, such as an increase in the viscosity and/or yield stress due to the stronger particle interactions. Change in the viscosity can affect the process ability of a particle suspension/dispersion and thus process yield. The lower the viscosity by diluting a suspension, the higher the transportability; but less amount of particles can be processed. On the other hand, increasing the particle concentration would increase the particle–particle interaction and the viscosity and thus lower the transportability and could result in the less process yield. In addition, so-called rheology modifiers can be

used to maintain a reasonable process yield in many industrial applications, including mining and paintings e.g., (Chana et al., 2007). Apparently, many companies dealing with particle suspension/dispersion systems are interested in increasing the particle/solid concentration to aim for a higher productivity as well as the effective waste/tailings management (Boger, 2009).

Understanding the suspension rheology is one of the key tasks for someone who deals with concentrated colloidal particle suspensions/dispersions, to properly maintain and manipulate the process ability and thus achieve a good yield of his/her products through a proper suspension/dispersion processing.

When particles are dispersed homogeneously in a dispersion/suspension, it exhibits less shear stress even at low shear rate that ensures its facile handling and manipulation. On the other hand, when a dispersion/suspension is composed of aggregate of colloidal particles, shear stress can be developed with the aggregation, and thus its handling and manipulation can be problematic; for example, higher energy consumption for mixing and transfer.

Fig. 4.6 (Barnes, 1977) shows the abovementioned aggregation/dispersion corresponding to the shear stress changing as a function of time of shear force application. The suspension behavior showing such change in flow curve is so-called thixotropy.

Yield stress is the minimum stress required for a viscoelastic material to flow and reflects the particle—particle interaction in a colloidal dispersion/suspension. Thus, it is quite useful to know/measure for each or important product to understand their flow behavior and give some indication about how to improve the flow behavior. Fig. 4.7 shows the graphical presentation of yield stress from the shear stress—shear rate relationship. The yield stress determination will be discussed in the following section.

3.1 Major principles of yield stress determination

The major principles of yield stress determination and unique and useful information a researcher can extract from yield stress curves (e.g., yield stress vs. the square zeta

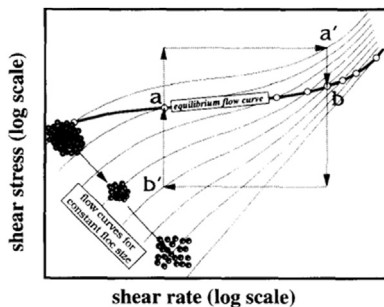
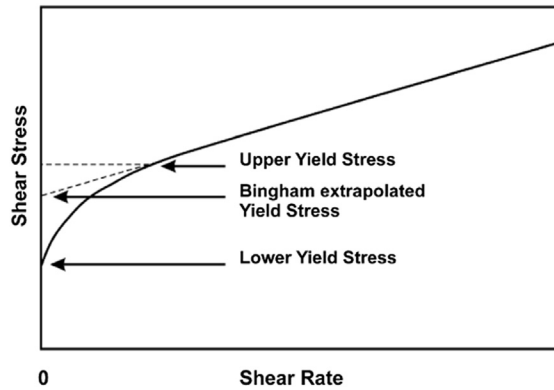
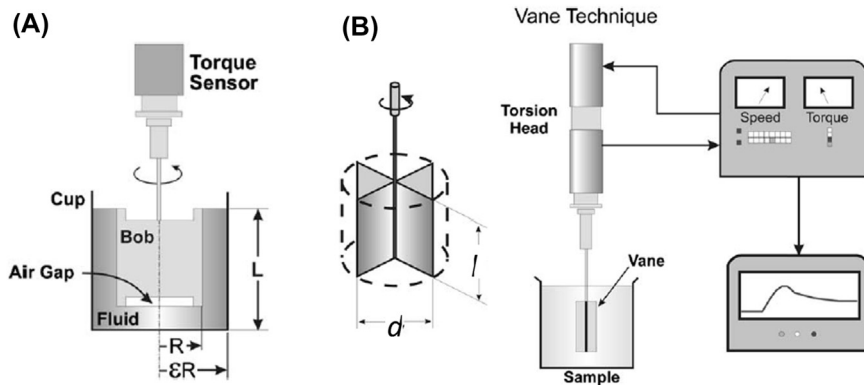


FIGURE 4.6

Flow curves of a flocculated suspension affected by change in microstructure (Barnes, 1977).

**FIGURE 4.7**

Typical shear stress–shear rate relationship indicating the yield stress (Boger, 2009).

**FIGURE 4.8**

(A) Couette geometry and (B) vane geometry (Boger, 2009).

potential, and other different plots) will be discussed as follows. In addition, the strong points and unique features of rheological measurement will be introduced.

Fig. 4.8A shows a Couette geometry composed of Bob (internal rotating part) and cup (external stationary part). In the gap between those two parts, a sample suspension is introduced. Fig. 4.8B shows a vane geometry with four plates that goes into a sample fed into a standard cup or another vessel.

By using both geometries, one can plot the shear stress as a function of shear rate, and the data are extrapolated from a linear region at high shear rates to the axis to determine what is called the Bingham yield stress that can be fit with the parameters [e.g., (Boger, 2009)]. The general caution that can obtain from Fig. 4.9 (Boger, 2009) is that using different geometries can provide different rheological measurement results especially the low shear rate region that is important for the yield stress

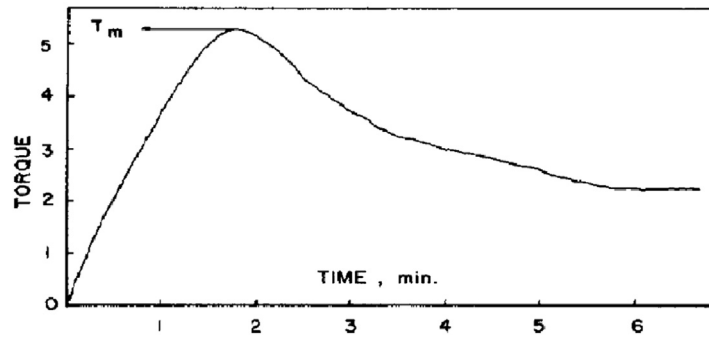


FIGURE 4.9

Flow curve for a paste sample measured with different geometries for yield stress determination (Boger, 2009).

determination while at the higher shear rate one can obtain the similar results regardless of the measurement geometries.

On the other hand, as indicated in Fig. 4.9 (Boger, 2009), different geometries could provide large deviation in the yield stress values obtained, a group of University of Melbourne initiated the development of direct and precise yield stress determination method using a vane geometry, and the raw torque value instead of using the shear stress converted from the torque. A reader interested in their series of investigation can find more detail information in (Dzuy and Boger, 1983b, 1983c).

As a summary, by using a vane geometry, one can determine the yield stress from the plot of torque as a function of time (Fig 4.10) and the use of the following equation (Boger, 2009):

$$T_m = \frac{\pi}{2} d^3 \left(\frac{l}{d} + \frac{1}{3} \right) \tau_y \quad (4.10)$$

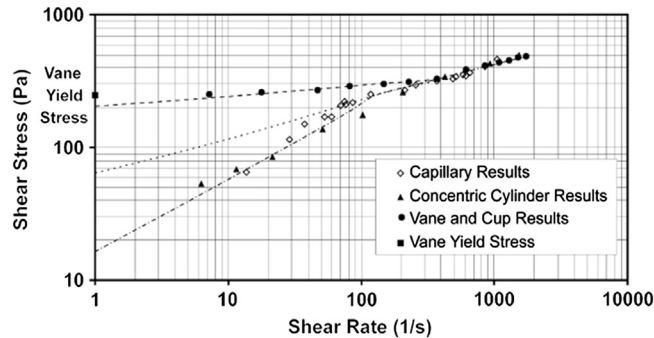


FIGURE 4.10

A torque as a function of time measured with a vane geometry (Dzuy and Boger, 1983c).

where T_m is the maximum torque value for a yielding sample, d is the vane diameter, and l is its height (Boger, 2009). This equation is valid if there are minimum end effects present with a large enough l/d vane.

3.2 Challenges and research gaps on suspension rheology of colloid systems

To test the applicability of the DLVO theory to a concentrated particle suspension system, rheological measurements can be made to determine the shear yield stress (τ_y) that is plotted as a function of the square of the zeta potential (ζ^2). If the DLVO interactions govern the particle–particle interactions, there should be the linear correlation between those two values as given below [e.g., (Firth, 1976)] and typical plots are given in Fig. 4.11A.

$$\tau_y = \tau_{y(max)} - k\zeta^2 \quad (4.11)$$

where τ_y is the shear yield stress, $\tau_{y(max)}$ is the maximum shear yield stress value at the isoelectric point (IEP), and k is a constant. This correlation can be explained by the stronger contribution of the van der Waals force over the weakest electrostatic repulsion at IEP ($\zeta = 0$) as depicted in Fig. 4.11B and 4.11C. Leong and Ong (2003) also claimed that the value of the intercept between the extrapolated line and ζ^2 axis indicates the square of critical zeta potential (ζ_c^2). That critical zeta potential shows the flocculation–dispersion transition. In other words, particles flocculate below this critical zeta potential, while they disperse above that due to the electrostatic repulsion.

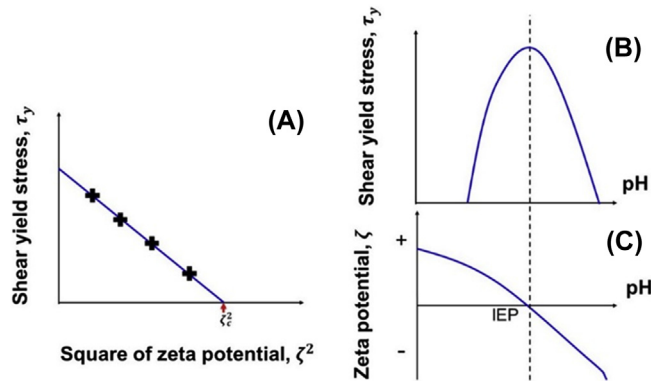


FIGURE 4.11

Typical correlation between the shear yield stress and the electrostatic interaction characterized by zeta potential for a homogeneous charged inorganic particle suspension. (A) The shear yield stress as a function of the square zeta potential, (B) the shear yield stress as a function of pH, and (C) zeta potential as a function of pH. IEP stands for the isoelectric point (Otsuki, 2018).

This approach was originally proposed by [Hunter and Nicol \(1968\)](#) to explain the contribution of the DLVO forces to the yield stress development, followed by the series of investigation performed by the same group ([Firth, 1976](#); [Friend and Hunter, 1971](#); [Firth and Hunter, 1976a,b](#)). Their aim was to correlate the electrokinetic behavior of colloidal particles explained by the surface potential (electrokinetic potential) with their suspension rheology. They derived the equation to correlate the yield stress as a function of the Hamaker constant (A_H) and the electrokinetic potential (ζ) which are responsible for the van der Waals force and the electrical double layer force, respectively. As they identified, the yield stress is negatively proportional to the square of zeta potential ([Eq. 4.11](#)). They also showed the usefulness and validity of yield stress plot as a function of the square zeta potential (or electrophoretic mobility, in the case of [Hunter and Nicol \(1968\)](#)). Although some of their plots were away from the majority, in general, the linear correlation between those two components were proven in their cases (i.e., kaolinite ([Hunter and Nicol, 1968](#)); polymethacrylate and polystyrene ([Friend and Hunter, 1971](#))). In the case of [Friend and Hunter \(1971\)](#), they also partly explained the potential reason of deviation from the linearity being based on the effect of temperature on zeta potential at its high range ($\zeta^2 = 1000 \text{ mV}^2$); but the data away from the linear trend at low zeta potential range ($\zeta^2 = 500 \text{ mV}^2$) remained unsolved.

Based on the model originally developed by [Kapur et al. \(1997\)](#), [Scales et al. \(1998\)](#) and [Johnson et al. \(2000\)](#) directly incorporated the suspension yield stress (τ_y) with the DLVO forces as [Eq. \(4.12\)](#) given below:

$$\tau_y = K_{struc} \left[\frac{A_H}{12H^2} - \frac{2\pi\epsilon_0\epsilon\kappa\zeta^2 \exp(-\kappa H)}{1 + \exp(-\kappa H)} \right] \quad (4.12)$$

where the terms in the square bracket accounts for the van der Waals and electrical double layer forces, K_{struc} is the network structural term depending on the particle size, the solid volume fraction, and the mean coordination number. In this [Eq. \(4.12\)](#), the basic idea behind is the same as [Eq. \(4.11\)](#) that explains the highest τ_y achieved with the weakest electrostatic repulsion at IEP.

[Scales et al. \(1998\)](#) also proposed the normalized yield stress (τ_N) as [Eq. \(4.13\)](#), with the assumption that all the structural (non-force) components are constant at a given volume fraction. Here, their model was developed for a simple particle suspension system without considering any additives and the value H is assumed to be an average interparticle distance.

$$\tau_N = \frac{\tau_y}{\tau_{y\max}} = 1 - \left(\frac{24\pi\epsilon_0\epsilon\zeta^2 H^2}{A(1 + \exp(\kappa H))} \right) \quad (4.13)$$

Their model explained well their experimental results with submicron size alumina particle suspensions, showing the same trend as shown in [Fig. 4.11](#) that $\tau_{y\max}$ was obtained at IEP.

[Johnson et al. \(2000\)](#) stated the potential limitation of [Eq. \(4.13\)](#) existing above the electrolyte concentration 0.01 mol/L that also correlates to the general caution to

the use of the DLVO theory, due to the following three reasons: (1) the electrical double layer overlap treatments of Hogg et al. (1966) based on the Gouy–Chapman description and used in the derivation of the above Eq. (4.13) can be significantly deviated from the solution of the Poisson–Boltzmann equation at high electrolyte concentrations; (2) high electrolyte concentration may lead the slight difference in the plane of shear and Stern planes and thus may significantly underestimate zeta potential (ζ) than diffuse layer potential (ψ_d) due to the steep drop of the potential. Therefore, the physical meaning of zeta potential is uncertain; and (3) the presence of high electrolyte concentration can change the magnitude of the Hamaker constant and thus can make the analysis complicated.

Harbour et al. (2007) later made a modification of the above Eq. (4.13) to obtain Eq. (4.14), assuming that the effective working distance for the van der Waals interaction, H_A , and that of the electrical double layer interaction, H_R , is different.

$$\tau_N = \frac{\tau_y}{\tau_{ymax}} = 1 - \left(\frac{24\pi\epsilon_0\epsilon\zeta^2 H_A^2}{A(1 + \exp(\kappa H_R^2))} \right) \quad (4.14)$$

Based on this modified equation, they also fit their experimental data with varying the H_A and H_R . Although their fitting was generally well achieved, some deviation from calculated values was also observed. In other words, some data were away from the linearity between the normalized yield stress and the square of zeta potential. They qualitatively explained the reason of this deviation potentially being associated with H or K ; but further modeling development to incorporate such nonlinearity was not performed. In addition, H_A and H_R appeared to be noticeably small (i.e., $H_A = 1.4\text{--}2.4$ nm, $H_R = 1.9\text{--}7.0$ nm) compared with the size of particles (i.e., less than 1%–2% of particle size $D_{50} = 300$ nm) they investigated. For example, using two equations previously proposed, Eq. (4.15) (Vesaratchanon et al., 2007)) and (4.16) (Woodcock and Bielefeld, 1985)), we can calculate the interparticle distance scaled by particle diameter (H/D) as a function of solid/particle concentration (ϕ) and compare with the H_A/D and H_R/D calculated from the reported values of Harbour et al. (2007), as shown in Fig. 4.12.

$$\frac{H}{D} = \left(\frac{0.52}{\phi} \right)^{\frac{1}{3}} - 1 \quad (4.15)$$

$$\frac{H}{D} = \left[\left(\frac{1}{3\pi\phi} + \frac{5}{6} \right)^{\frac{1}{2}} - 1 \right] \quad (4.16)$$

As shown in Fig. 4.12, the trend estimated by using those two equations are similar (i.e. decrease in the interparticle distance with particle concentration) while the H_A/D and H_R/D are far smaller than the values identified by the two equations (e.g. H_A/D , $H_R/D < 0.01$ vs. H/d calculated using Eq. 4.15 or 4.16 > 0.1 at 0.25 particle volume fraction). This suggests that there must be some degree of overestimation in the modeling of Harbour et al. (2007), and thus that point might be further studied and clarified to have a practically reasonable distance.

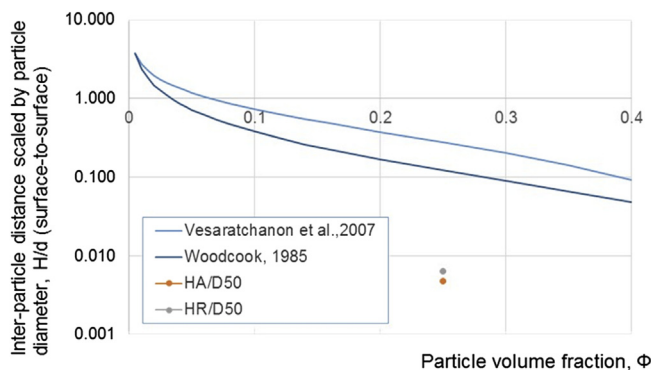


FIGURE 4.12

Interparticle distance scaled by the particle diameter, calculated using the equations of [Vesaratchanon et al. \(2007\)](#) and [Woodcock and Bielefeld \(1985\)](#), compared with the calculated values of H_A/D_{50} and H_R/D_{50} , using the values reported in [Harbour et al. \(2007\)](#) given in dots ([Otsuki, 2018](#)).

3.2.1 Non-spherical/platy charged particle suspension

3.2.1.1 Particle size distribution

In real colloidal dispersions/suspensions, there should be distribution of physical properties, including the distribution of particle size. It is often referred as the polydispersity whose influence on the properties of spherical particle dispersion can be described in the following form, so-called the Schultz distribution ([Dickinson, 2015](#)):

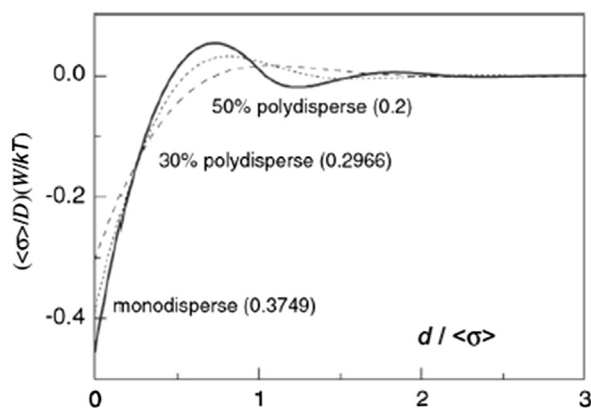
$$f(\sigma) = \frac{1}{\Gamma(z+1)} \left(\frac{1+z}{\sigma} \right)^{1+z} \sigma^2 \exp \left[\frac{-(z+1)\sigma}{\sigma} \right] \quad (4.17)$$

where the average diameter is σ , while the polydispersion degree is expressed as the standard deviation $(z+1)^{-\frac{1}{2}}$ and $z = \infty$ corresponds to a monodisperse system.

[Fig. 4.13](#) shows that the increase in particle polydispersity provides less feature particle interaction energy due to the reduction of interaction energy that in other words the energy dissipates. For monodisperse particles, even with higher particle concentration, there is a noticeable peak indicating the particle interaction present in the system.

Similar case was also reported by [Otsuki et al. \(2018\)](#) who studied the effect of H_2O/D_2O contrast variation of the scattering patterns obtained by polydisperse colloidal suspensions, showing the feature less scattering curves.

When a colloid has a complex structure, such as a protein molecule shown in [Fig. 4.14](#) ([Hattori et al., 2001](#)), it can create the heterogeneity in physical and chemical properties. Here the example given discusses the surface charge heterogeneity present in an albumin molecule at pH 7. Such heterogeneity can create the heterogeneity in terms of molecule–molecule and molecule–particle interaction and

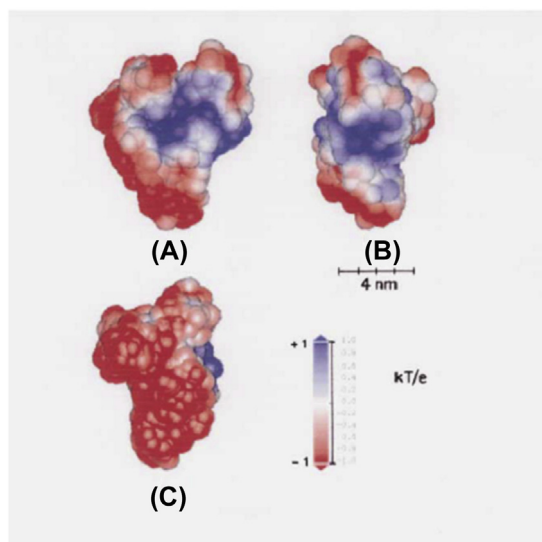
**FIGURE 4.13**

Effect of polydispersity on the interaction energy as a function of the surface-to-surface separation distance (Dickinson, 2015).

Charge Density on Bovine Serum Albumin at pH 7

BLUE = +VE CHARGE

RED = -VE CHARGE

**FIGURE 4.14**

Surface charge distribution of bovine serum albumin at pH 7 (Hattori et al., 2001).

Table 4.3 Summary of governing forces and important information relevant to couple colloidal forces and suspension yield stress in a charged inorganic colloidal particle suspension (Otsuki, 2018).

	Particle type					
	Spherical		Non-spherical	Dissimilar / mix particle		
	DLVO	DLVO+Non-DLVO		Spherical-spherical	Spherical-Non-spherical	Non-spherical-Non-spherical
Governing forces for yield stress development	$(+)F_{VDW}(-)F_{EDL}$	$(+)F_{VDW}(-)F_{EDL}$ $(+)F_{Non-DLVO}$ (hydrophobic+hydration+steric+...)	$(+)(F_{VDW})$ $(+)F_{EDL}^*$	$(+)F_{VDW}(-)F_{EDL}$	$(+)F_{VDW}(-)F_{EDL}^{**}$	
Particle surface charge distribution	Homogeneous	Homogeneous	Heterogeneous	Homogeneous+homogeneous	Homogeneous+heterogeneous	Heterogeneous+heterogeneous
Limitation/ boundaries	Salt concentration recommended to be below 1×10^{-2} M; no additives concerned	Additional analysis required; but which method, how and what to analyse not standardized	Separate determination of zeta potential of face and edge can be challenging. No standardized modelling developed yet.	No model development specifically designed to such systems yet.		
Example of case studies (reference numbers given)	42, 49	75, 76, 80	67, 69, 71-74	11, 83	84, 85**	

F_{VDW} = van der Waals force, F_{EDL} = electrical double layer force, $F_{Non-DLVO}$ = non-DLVO forces, (+) = additive contribution to the yield stress development, (–) = reductive contribution to the yield stress development. *Contribution from the electrical double layer force was not properly justified yet.

**General trend reported with significant scattering and deviation from the linearity between shear yield stress and the square of zeta potential.

thus change in the macroscopic behavior as a food colloid dispersion/suspension. This heterogeneity and change can be severe with increasing the concentration of those molecules/particles. Development of models explaining those interactions and thus predicting the macroscopic suspension behavior via potential/force calculation would be of significant help for someone to formulate or manipulate such complex colloid systems.

Otsuki (2018) reported the research gaps identified in the yield stress–DLVO forces coupling, and his summary is given in Table 4.3. It indicates that other than spherical similar particle suspension systems there are so many opportunities available in the future research works as the systems increase their complexity and heterogeneity. One of the challenges was non-spherical particle system where there is no standard models developed yet. Fig. 4.15 shows the potential charge heterogeneity can be assigned between face and edge of a clay particle in alkaline pH where separate determination of surface charge can be a challenging task in terms of creating a model explaining the behavior of different clay particle suspensions (Otsuki, 2018).

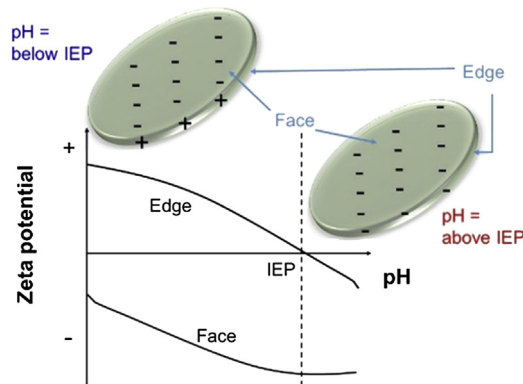


FIGURE 4.15

Typical zeta potential curves of edge and face of a clay particle as a function of solution pH. Particle drawings show the type of charge (i.e., negative, positive) carried on the edge and face below and above IEP (Otsuki, 2018).

4. Summary and future perspectives

In this article, the issues associated with colloidal dispersions/suspensions were first discussed in relation to the formulation with increasing their concentration that is a general trend in many of colloidal processing industries. The DLVO theory was then introduced to evaluate the particle–particle interaction in colloidal systems and their stabilities with some applications given. In terms of characterization methods, several suspension rheology methods were introduced, including their theoretical and experimental background together with their applications to concentrated colloid dispersions/suspensions. As a part of this article, a series of investigations to apply the DLVO theory to explain the forces as well as microscopic particle interaction and macroscopic suspension behavior within such colloidal particle dispersions/suspensions was reviewed, and the associate basic phenomena were introduced. Some of such investigations with examples of different suspension types and advanced theories were illustrated. Because there is a growing interest in understanding the behavior of complex colloid particle systems, such as multi-colloid particle suspensions, further investigation and development of characterization of such complex colloid dispersions/suspensions with flexible capacity to incorporate with different types of particle suspensions to better understand and explain such systems with extracting the science of particle interaction and its reflection to enhance particle/suspension processing is highly recommended. Such efforts hold a good potential to create a new research field and to provide useful insight and suggestions to industry about characterization and dispersion/coagulation of colloidal particles and their suspensions for better processing.

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Rheology of polymer nanocomposites

5

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Abstract

Nowadays, more and more interests are focused on the development of nanocomposite materials. Determining their rheology is an essential way to simulate the real processes and complete materials characterization. The present chapter underlines the properties of differently used nanofillers in literature before cited the commonly adopted preparation and technique to obtain the nanocomposite materials. On the other hand, the focus is on the techniques and equipment used to characterize the rheological properties and what extent the state of dispersion and nanoparticle morphology affect the rheological behavior. Finally, the emphasis is given to the theory and models describing the nanocomposite rheology including Hershel Bulkley and Bingham models.

Keywords: Bingham model; Hershel Bulkley model; Nanocomposites; Nanofillers; Rheological properties; Rheology.

1. Introduction

Nowadays, the daily use of polymer materials in various industries such as automotive or packaging requires progress and innovations to improve the properties of these materials and increase the diversification of their fields of application. The incorporation of reinforcing agents in the polymers leads to so-called composite materials and makes it possible to respond effectively to economic and practical expectations. The micron and nanometric size of the used reinforced fillers in the polymeric matrices allows classifying them to composite or nanocomposite, respectively. Indeed, a problem with the use of traditional micron size fillers in polymers is that the particles may be too large. In this case, they introduce the embrittlement of the material and opacification by inducing critical damage under mechanical stress.

For this reason, composites with a nanometric charge have been increasingly studied since the 2000s. The use of nanoparticles in nanocomposites generally allows not to damage the material and in some cases to avoid opacification of it. With a low level of nanofillers, it is possible to obtain an overall improvement in the properties of the materials (Hu et al., 2006) (Bin et al., 2003). The transition

from micro- to nanoparticles leads to changes in physical and also chemical properties. These changes can be attributed to the increase in the surface to volume ratio of the reinforcing and/or its exceptionally high aspect ratio. The large surface area of the nanoparticles allows for better interaction with the polymer during compounding. In terms of application of these materials, it will be interesting to give the examples of energy saving in electro catalyst in batteries, lightweight materials for less fuel consumption, artificial joints, food packaging, marine application, erosion and corrosion application, and environmental protection.

To better understand the structure and relationships responsible for the strengthening of polymers by particles, several works on the rheological behavior of nanocomposites, i.e., macroscopic viscoelastic behavior, have been made toward these objectives (Li et al., 2003) (Hyun et al., 2001) (Hu et al., 2006). The rheology is thus placed at the border between structural determination and physical properties of the nanocomposites; moreover, this technique is often the key in the understanding and the improvement of the implementation. In other words, the rheological study is generally conducted to provide useful guidance for overcoming potential difficulties resulting from significant changes in the viscoelastic melt properties observed in the nanocomposites (Lim and Park, 2001; Krishnamoorti and Giannelis, 1997; Galgali et al., 2001) and to study the internal microstructures of nanocomposites including the state of dispersion and distribution of the nanoparticles.

This chapter aims to contribute to the understanding of the phenomena governing the physicochemical and particularly rheological behavior of nanocomposites. Before detailing this part, the properties of nanofillers, their surface modification, and the procedures used to obtain the nanocomposite are also investigated. Afterward, a section is dedicated to show how the understanding of the rheological behavior of the polymeric nanocomposites helps to characterize the state of dispersion of nanoparticles. The final section highlights the most used modeling approaches presenting rheological behaviors.

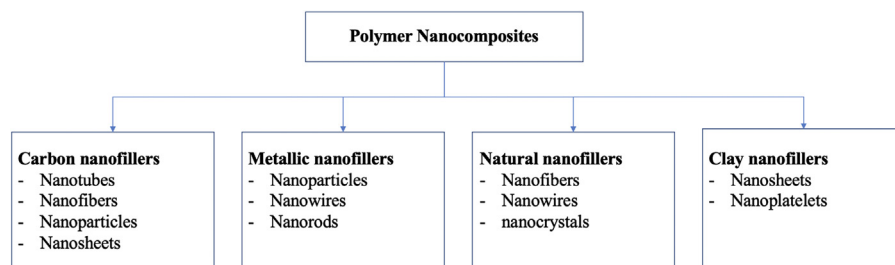
2. Polymer nanocomposites

2.1 Nanofiller properties in polymer

The most important attribute that defines the nanofiller is size. Indeed, nanofillers are tiny materials having a nominal diameter of less than 100 nm (0.1 μm) (Khan et al., 2017).

The nanoparticles exist in different forms, such as fibers (one-dimensional), sheets (two-dimensional), or spheres (three-dimensional), but have at least one dimension between 1 and 50 nm.

Polymeric matrix nanocomposites can be classified into four important subfamilies according to the type of nanofillers embedded in the matrix and their scientific interest as illustrated in Fig. 5.1.

**FIGURE 5.1**

Classification of polymeric matrix nanocomposites.

2.1.1 Carbon nanofillers

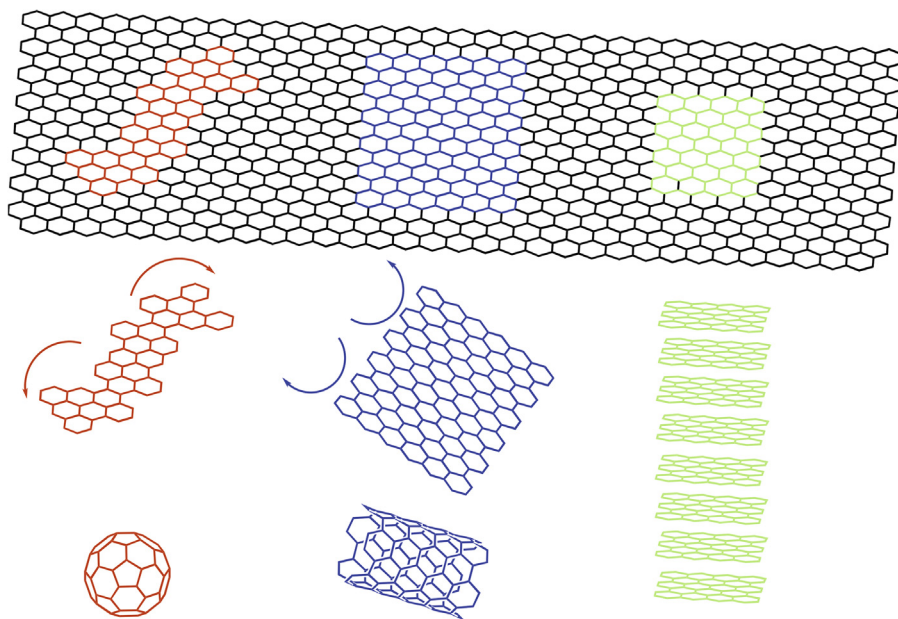
The nanofillers based on carbon are particularly interesting because they are able to give the materials an electrical conductivity in addition to improving the traditional properties which extend the range of possible application with these nanocomposites (Thomassin and Jérôme, 2013). The carbon nanofillers of all shape could be found as sphere or nanoparticles (carbon black, fullerene), nanotubes (carbon nanotubes), nanosheets (graphene), and carbon nanofibers which are cylindrical nanostructures with graphene layers arranged as stacked cones, cups, or plates.

Carbon black (CB) derives from the incomplete combustion of fossil fuels, wood, and biomass (Goldberg and, 1985). The various CBs are in the form of powders consisting of spherical particles. It is used in various targets to improve the properties of the filled nanocomposite. Indeed, H. Yang et al. (Yanget al., 2015) found that the insertion of CB in polypropylene/carbon fiber composite dramatically enhances the thermal stability, flame retardancy, and electrical conductivity.

Carbon nanotubes are composed of one or more sheets of carbon atoms wound on themselves forming a tube. The tube may or may not be closed at its ends by a half sphere. It is characterized by its extraordinary mechanical, thermal, and electronic properties, which allow it feature like an outstanding material (Hu et al., 2006). Indeed, its elastic modulus can reach 1 TPa, its thermal conductivity may be twice as high as that of diamond, and the electrical current carrying capacity may be 1000 times as that of copper wires (Bin et al., 2003).

Graphene or carbon nanosheet (CNS) is a carbon nanofiller consisting of a single layer of carbon atoms arranged in a honeycomb lattice (Fig. 5.2). These sheets are then spontaneously superimposed on each other, and their stacking has termed graphite. The addition of graphene in a polymer makes it a conductor and increases the thermal conductivity, thermal stability, mechanical properties, and dimensional stability of the polymer (Kim et al., 2013) (Ashjara and Oshaghi, 2014).

Carbon nanofibers (CNFs) are cylindrical structure composed of CNS which are organized under a precise geometry. CNS is often derived using metallic catalysts used for the conversion of carbon containing gases (DE JONG and GEUS, 2000). Generally, two different types of fibers may be grown: parallel and fishbone fibers. The resulted graphitic CNF directly depends on the nature of the

**FIGURE 5.2**

Representation of carbon nanofillers: (A) graphene; (B) carbon black; (C) carbon nanotubes; and (D) graphite.

used metal. When these graphitic materials are inserted and well dispersed in the polymer, the overall strength, electrical, and thermal conductivity are improved (Rodriguez et al., 1994) (Tibbetts et al., 2007).

In addition, H. Kim et al. (Kim et al., 2013) reported that a combination of different carbon fillers can lead to synergetic physical property gain for polymers. This effect is due to the creation of the bridging interaction between hybrid graphitic nanofillers; therefore, some composite properties as thermal conductivity are enhanced (Yu et al., 2008).

2.1.2 Metallic nanofillers

The metallic nanofillers have been of the interest to researchers for over a century and are widely used in engineering and biomedical sciences. Different forms of these nanofillers are used, such as metallic nanoparticles, metallic nanowires, and metallic nanorods. Their incorporation in insulating polymeric matrices improves their electrical conductivity, their mechanical properties in term of hardness, tensile, and flexural properties, and their impact strength and tribological behavior (Rybak et al., 2010) (Divya and Suresha, 2018).

2.1.3 Natural nanofillers

Nanoscale natural resources are what is meant by natural nanofillers. The most interesting aspect of incorporation of these nanofillers in polymeric matrices is

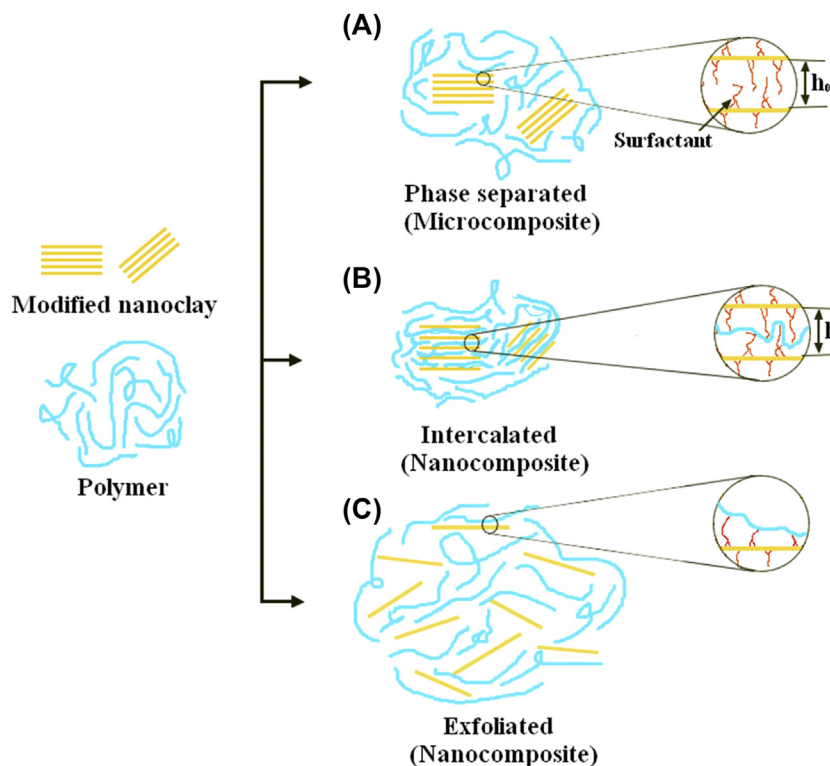
their biodegradability. However, the weak interfacial attractions between the matrix polymer and these fibers and high characteristics moisture absorption properties of many natural fibers remain the drawbacks to overwhelm in order to not hamper their applications. Natural nanofibers, natural nanowires, and natural nanocrystals are the used forms of natural nanofillers. Their incorporation in polymeric matrices, especially nanoparticles, enhances the physical and mechanical properties of polymer matrix (Saba et al., 2014) (Siqueira et al., 2010).

2.1.4 Clay nanofillers

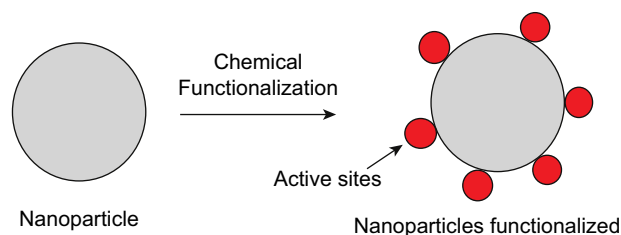
Nanoclays or clay nanofillers are nanoparticles of layered mineral silicates. Their incorporation in the polymeric matrix can lead to different types of morphology depending on the ability of polymer chains to penetrate between clay galleries (the notion of intercalation) or to break up the stacked structure of clays by delamination of sheets (the notion of exfoliation). Indeed, when the organic polymer has interacted with inorganic clay (unmodified clay), the polymer is unable to intercalate within the clay layers and the clay is dispersed as aggregates or particle with layers stacked together within the polymer matrix. The obtained composite structure is considered as “separated phase.” Thus, the polymer/clay composites are classified in the range of traditional microcomposites. Regarding the intercalated nanocomposite, it is formed when one or more polymer chains are inserted into the interlayer space, which cause the increase of the interlayer spacing, but the periodic array of the clay layer is still existing. The presence of polymer chains in the galleries decreases the electrostatic forces between the layers but it is not totally dissolved. In this configuration, a well-ordered multilayer hybrid morphology with a high interference interaction consisted of polymer chains and clay layer is obtained. Regarding the exfoliated or delaminated nanocomposite, it is resulted when the insertion of polymer chains into the clay galleries separates the layers one another and individual layers are dispersed within the polymer matrix. At all, when the polymer chains increase the interlayer spacing more than 80–100 Å, the exfoliated structure is obtained. As results, a high aspect ratio is obtained and lower clay content is needed for exfoliated nanocomposites due to the good dispersion of individual clay layers. Moreover, the large surface interactions between polymer and clay are the most significant improvements in polymer. Fig. 5.3 illustrates the main morphologies of reference frequently evoked in the literature. Jo et al. (Jo et al., 2008) reported that the incorporation of treated nanoclays (montmorillonite (MMT)) to the resin concrete enhances the strength and modulus in compression of concrete. In addition, an improvement is known in elastic modulus of the nanocomposite by the addition of nanoclays (MMT).

2.2 Surface modification of nanofillers

The interface between matrix and reinforcement play an important role in the properties of nanocomposites. A discontinuity of one or more material parameters (elastic moduli, strength, and chemical potential) occurs due to the lack of thermodynamic equilibrium at the matrix and reinforcement interface. Moreover, the

**FIGURE 5.3**

Main morphology of nanocomposite: (A) microcomposite, (B) intercalated, and (C) exfoliated.

**FIGURE 5.4**

Chemical modification of nanoparticle surface.

matrix and the nanofillers are not in thermodynamic equilibrium at the interface, the specific surface area and high surface energy occurred the agglomeration. To improve the interfacial interactions between the inorganic particles and the polymer matrix, the nanofiller surfaces are chemically modified (Fig. 5.4). Therefore, the nanofillers are stabilized against agglomeration, can avoid homogeneity and

compatibility problems, and become compatible with another phase to enable their self-organization.

In addition, the surface modifications are applied to nanomaterial for several reasons including the limitation in the applications of these nanomaterials because of their restricted behavior in different solvents. Moreover, the surface modifications of nanomaterials help to tune their properties to suit different applications in the field of nanotechnology, because surface properties determine the interaction among the components, as well as the solubility and agglomeration behavior in different solvents. Generally, the main aim of chemical modification of nanoparticle surface is to make nanomaterial-gained hydrophilic, hydrophobic, conductive, or anti-corrosive properties.

2.3 Preparation and chemical processing techniques

Preparing nanocomposite materials meant that some challenges had to be taken up including preventing nanocomposite from agglomeration, overcoming the huge surface energy which is a result of enormous surface area or large surface to volume ratio, controlling morphology, and obtaining desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure desired physical properties. There exist different techniques of polymer nanocomposite synthesis. In this section, three methods will be detailed especially in situ polymerization, solution processing, and melt compounding.

2.3.1 In situ polymerization

First of all, in situ is a Latin phrase which translates literally to “in position.” This technique involves a chemical reaction resulting in the formation of a very fine and thermodynamically stable reinforcing phase within a matrix. The in situ polymerization is the main technique for the preparation of thermosetting nanocomposite which cannot be synthesized by melt blending (technique will be detailed in following sections). Their processing requires that the nanoparticles are dispersed in a liquid monomer or relatively low-molecular-weight precursor and in their solution. When a homogeneous mixture is formed, initiator is added and it is exposed to appropriate source of heat, light, etc. (Fig. 5.5). It is worth to note that the nanofillers are dispersed through ultrasonication in the prepolymer.

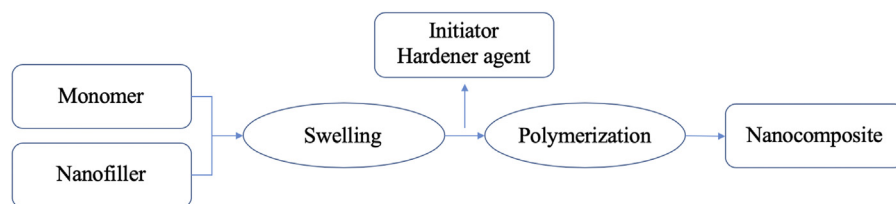
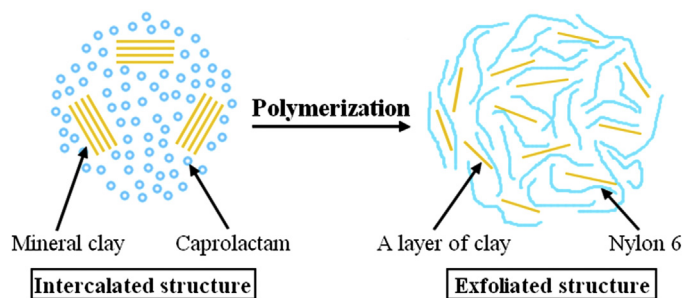


FIGURE 5.5

Diagram showing the in situ polymerization technique.

**FIGURE 5.6**

Preparation of nanocomposites nylon-6/clay by in situ polymerization.

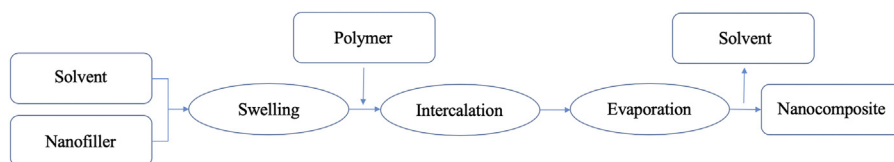
As the polymerization progresses, the viscosity of the solution increases and the polymer grows and wraps around the dispersed nanofillers. As a result, higher interfacial strength as nanofillers interact with the growing polymer, thus forming stronger nanofiller–polymer bonds via noncovalent or covalent interactions which lead to obtaining composites with enhanced mechanical, electrical, and tribological performances (Coleman et al., 2006).

The main advantages of this processing method involve the thermodynamic compatibility at the matrix–reinforcement interface; in addition, the reinforcement surfaces are likely to be free of contamination. Therefore, the stronger matrix dispersion bond can be achieved. This technique is considered important for the preparation of insoluble and thermally unstable polymer composites, which cannot be processed by solution or melt processing, which will be detailed in the following sections.

Various studies were treated by this technique, including the in situ polymerization of the ϵ -caprolactam in MMT, nanocomposite nylon/MMT (Fig. 5.6) (Usukiet al., 1993) (Okada and Usuki, 1995), epoxy nanocomposite (Lan et al., 1995), and nanocomposites poly(methyl methacrylate) (Coleman et al., 2006) (Okamoto et al., 2000).

2.3.2 Solution processing

This method is also termed as exfoliation/adsorption. This preparation mode consists to mix the polymer and the nanofiller in the same solvent and then remove it. To optimize this technique, it is wise to use a solvent which is both the good solvent for the polymer and which makes it possible to swell (exfoliate) the nanofiller. This method is divided into three major synthesis stages (Fig. 5.7). The nanofiller is swollen in the solvent, then the polymer is introduced into, finally, the solvent is removed by evaporation. This is a technique used for polymers without or with low polarity. However, the need for the use of the solvent is the main disadvantage of this method, which is in total opposition to today's environmental challenges and industrial applications. Nevertheless, it is particularly suitable for water-soluble polymers, which make it possible to use water as a solvent (Vaia et al., 1997) (Ogata et al., 1997).

**FIGURE 5.7**

The technique of solvent processing.

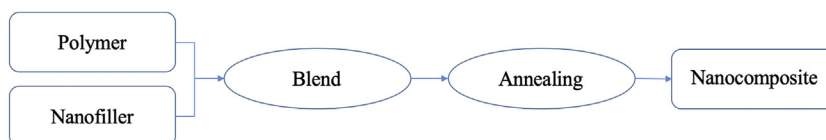
From a thermodynamic perspective, the loss of entropy due to the intercalation of the chains and thus to their confinement is compensated by the gain coming from the desorption of numerous solvent molecules (Theng, 1979), which favors the formation of the nanocomposite. It should also be noted that this method was effectively used in the case of poly(ethylene oxide) (Aranda and Ruiz-hitzky, 1992) (Wu and Lerner, 1993) (Hyun et al., 2001), (Choi et al., 2001) using different more or less polar solvents, but also with many other polymers.

2.3.3 Melt compounding

Unlike the previous processing, this synthesis method has many advantages that the industrial sector continues to operate and develop. It involves mixing directly the nanofillers to the polymer above the glass transition temperature (Fig. 5.8). The low cost of this method remains its main advantage.

It is of great interest because it can work in the absence of a solvent and not to modify the process for the usual use of thermoplastic polymers. The separation is done by diffusion of the macromolecular chains in the space between the sheets (for example, in the case of graphene) and by a conventional mixing process, such as twin screw extrusion. However, this method requires special conditions, especially the compatibility between the matrix and the nanofillers. During processing, the shear stress is induced in the polymer melt by viscous drag and is used to break down the nanofiller aggregates. As a result, the homogeneous and uniform nanofiller dispersion is appeared in the polymer matrix.

Taking the example of the clay, the organophilic clays are the using clay for this technique, although recent studies have shown that the use of untreated clay for the polypropylene matrix is possible (Kato et al., 2004). The first work on this technique has been made by Vaia et al (Vaia et al., 1993, 1995; Vaia and Giannelis, 1997a, 1997b). They have shown experimentally that the macromolecular chains of a polystyrene can diffuse by a simple annealing inside the space between the layers,

**FIGURE 5.8**

The technique of melt compounding.

with an interlamellar distance of the order of 2.13 nm. The penetration of the polystyrene chains leads to a final interlamellar distance of the order of 2.83 nm. This therefore indicates that the separation of the agile sheets is possible from a polymer in the molten state.

In comparison with in situ polymerization and solution mixing methods, the melt blending technique (extrusion) is the most answered way on an industrial scale for the preparation of polymer nanocomposite systems. However, it is not yet widely used for the preparation of polymeric nanocomposites/graphene due to the difficulty of handling graphene nanosheets presented during the blending processing. Indeed, the low density and large surface area of the graphene nanosheets make it very difficult to incorporate them into the polymer matrices, via the extrusion approach (feeding difficulty in the extruder).

3. Rheology of nanocomposites

Rheology is the deformation and material flow study. It is dedicated to the study of viscoelastic materials that include both liquid and solid properties; we talk about soft material. The rheological behavior of the reinforced polymers depends on many parameters, such as the nature of the fillers (size, shape), the concentration, and the interactions between the fillers and between the polymer and the fillers. These parameters cause not only an increase in viscosity but also particular phenomena such as the existence of a flow threshold, a thixotropic, shearing thinning or shearing thickening behavior. In the case of nanocomposites, all the rheological characteristics of the conventional filled polymers are generally observed. However, because the size of the charges is extremely small, the surface developed with the polymer matrix is therefore very large (Knauert et al., 2007). To obtain a reproducible measurement, independent of a human factor such as the altitude of the flow cut, the gradient (of shear, stress, or strain) applied to the fluid must be known. For this, appropriate equipment must be used.

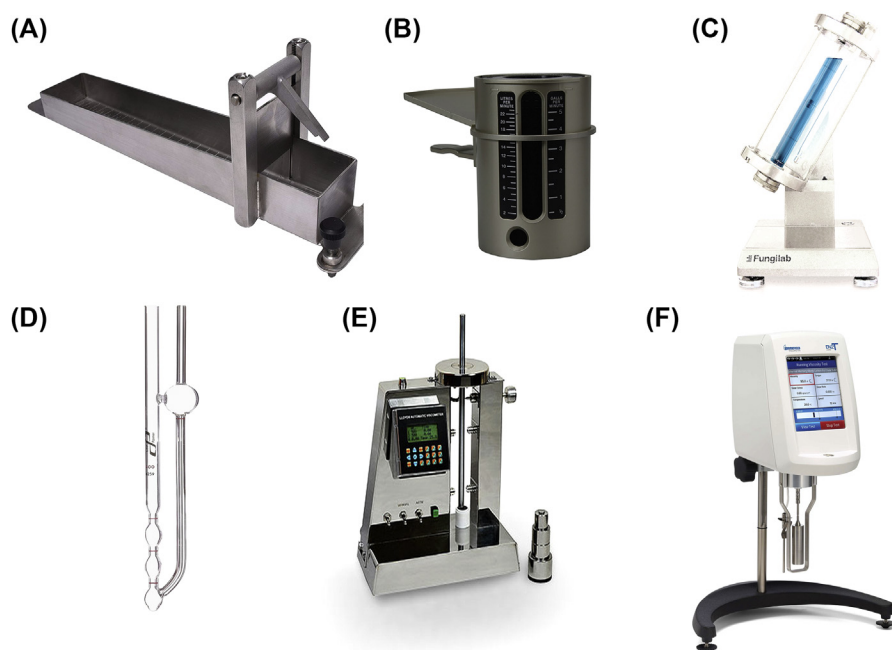
3.1 Techniques and equipments to characterize the rheological properties

Various devices allow the polymer viscosity measurements. These are kinematic viscometers or rheometers.

3.1.1 Kinematic viscometers

Kinematic (or gravity) viscometers are numerous and are still widely used today. A summary of different instruments is presented Fig. 5.9.

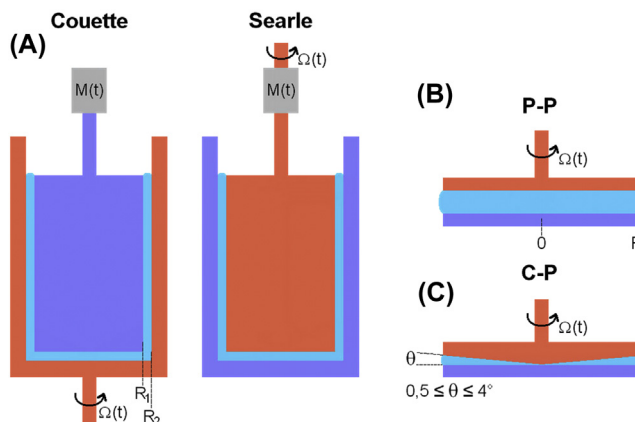
The Bostwick Consistometer (Fig. 5.9A) measures the distance traveled by the fluid in a limited time. This device is useful for mixtures containing large pieces (solid–liquid mixtures, etc.) (Balmforth et al., 2007). The flow cup (Fig. 5.9B), used in ancient times to measure time, now measures the viscosity of oils or paints

**FIGURE 5.9**

(A) Bostwick Consistometer, (B) flow cup, (C) viscometer with ball drop, (D) capillary viscosimeters, (E) Laray viscometer (falling stem), (F) rotary viscometer (Brookfield).

especially in the automotive industry (Balmforth et al., 2007). The falling ball viscometer (Fig. 5.9C) uses the fact that the ball's falling time is a function of the viscosity of the liquid. Temperature control is often available on these devices (Cho et al., 1984). The capillary viscometers (Fig. 5.9D), of various geometries, are based on the following principle: the flow time of a low viscosity liquid in a capillary is a function of its viscosity (Philippoff and Gaskins, 1958). The falling stem viscometer or Laray viscometer (Fig. 5.9E) is used for fluids with very high viscosities; in its operation, a central axis descends under the influence of a weight then forcing the liquid to flow (Erhan et al., 1992). The Brookfield rotary viscometer (Fig. 5.9F), still widely used in industry, does not measure a kinematic viscosity or a dynamic viscosity but a relative viscosity; indeed the shear rate applied to the fluid is not known, the fluid is not confined in a known geometry (Cappello et al., 1998).

Viscosity is often studied relatively, especially in industry, where sometimes only reproducibility counts. That is why we still find today consistometers at jam makers or drains in the automotive industry. However, to obtain a reproducible measurement, independent of a human factor such as the altitude of the flow cut, the gradient (of shear, stress, or strain) applied to the fluid must be known. For this, a rheometer is used.

**FIGURE 5.10**

Rheometer geometries: (A) Couette, (B) plane–plane, (C) cone–plane.

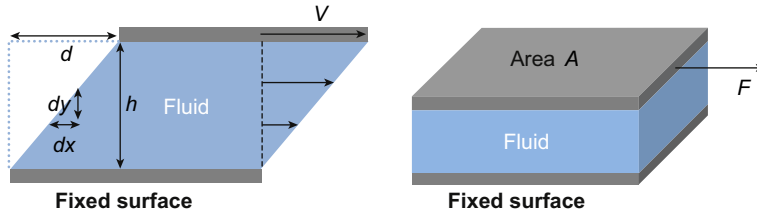
3.1.2 Rheometers

The rheometer makes it possible to directly determine the viscosity, as well as the other rheological parameters, thanks to the measurement of the torque produced by a deformation (rotation) imposed for very precise geometries (for example: parallel plates, cone-plane, Couette, etc.). The latter consists of a motor driven in torque or speed, the deflection angle of the motor axis relative to the control being generally measured optically (Meissner and Hostettler, 1994). At the end of the motor axis, different heads, corresponding to different geometries can be mounted on the device (Fig. 5.10). The cylindrical geometry (Couette or Searle according to the rotatable portion) is suitable for low viscosity or in some cases mixtures having large grains (Fig. 5.10A). It is not recommended for very viscous pastes because of the possible formation of air bubbles. The plane–plane geometry (Fig. 5.10B) is suitable for the characterization of pastes or gels. It allows a high air gap required for materials comprising, for example, large particles. The cone–plane geometry (Fig. 5.10C) is the only geometry that meets the criterion of constant shear rate. It allows the characterization of homogeneous materials with particles smaller than 5 μm (Geraud et al., 2013).

3.2 Rheological investigation

For the viscosity measurement, the so-called “two-plate” model is used. It defines the space in which a mechanical stress will be applied to the fluid. In this model, the soft material is trapped between two surfaces; one is fixed, the other is mobile and moves at a constant speed. A shearing motion is then applied to the material to study its ability to flow (Fig. 5.11) (Kavanagh, 1998).

The macroscopic shear strain experienced by the fluid is defined as the horizontal displacement of the upper surface “d,” divided by the interplate distance “h.”

**FIGURE 5.11**

Shear in the case of the two-plate model.

We then define the local shear strain “ γ ” by the equation [Eq. \(5.1\)](#) ([Kavanagh, 1998](#)). Shear deformation is constant if at all points, “ γ ” is equal to the macroscopic deformation. This definition is used very frequently in rheology, especially when using the two-plate geometry ([Kavanagh, 1998](#)).

$$\gamma = \frac{dx}{dy} \quad (5.1)$$

[Eq. \(5.2\)](#) defines the shear rate also known as “shear”; it is the derivative with respect to the time of the deformation. In practice, it is often defined as the quotient of the velocity of the upper surface divided by the thickness of the fluid sample (velocity gradient) ([Kavanagh, 1998](#)).

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{V}{h} \text{ (s}^{-1}\text{)} \quad (5.2)$$

Between the two solid surfaces, the material can be considered as a stack of layers capable of sliding relative to each other under the action of shear, showing stresses between each layer. We are talking about shear stress “ τ ” ([Eq. 5.3](#)), the quotient of the force “ F ” applied to the upper plate, and the area under the plate A ([Fig. 5.5](#)) ([Kavanagh, 1998](#)).

$$\tau = \frac{F}{A} \text{ (Pa)} \quad (5.3)$$

A number of conditions are necessary for the use of the two-plate model ([Kavanagh, 1998](#)):

- No slip at fluid/solid interfaces (fluid adheres to both plates)
- Laminar flow (no turbulence)
- Constant shear rate (this is the measurement assumption made when using rheometers)

In an oscillatory shear flow, sinusoidal pulsation deformation (or stress) “ ω ” is applied. We measure a stress (or deformation) itself sinusoidal pulsation “ ω ” insofar as the amplitude of the stress is low. If the deformation is of the form ([Eq. 5.4](#)) ([Kavanagh, 1998](#)) ([Sawpan et al., 2011](#)):

$$\gamma = \gamma_0 e^{i\omega t} \quad (5.4)$$

The stress response is written in the linear domain by Eq. (5.5) (Kavanagh, 1998) (Sawpan et al., 2011):

$$\tau = \tau_0 e^{i(\omega t + \delta)} \quad (5.5)$$

δ being the loss factor. The complex shear modulus G^* is defined by Eq. 5.6 (Kavanagh, 1998) (Doraiswamy et al., 1991):

$$G^* = \frac{\tau}{\gamma} = \frac{\tau_0}{\gamma_0} e^{i\delta} = G' + iG'' = \sqrt{G'^2 + G''^2} \quad (5.6)$$

The loss factor is the relationship between the loss modulus “ G'' ” and storage modulus “ G' ” and is given by the following equation (Eq. 5.7) (Ravanagh, 1998) (Arrakhiz et al., 2013):

$$\tan \delta = \frac{G''}{G'} \quad (5.7)$$

G' represents the real part of G^* . It is the conservation module and it characterizes the response in phase with the deformation. It is associated with the elastic response. G'' is the imaginary part of G^* . It is in quadrature phase with deformation and characterizes the viscous response (Ravanagh, 1998) (Doraiswamy et al., 1991):

The complex viscosity η^* is defined by Eq. 5.8:

$$\tau(t) = \eta^* \dot{\gamma} \text{ and } \eta^* = \frac{\tau_0 e^{i(\omega t + \delta)}}{\gamma_0 i \omega e^{i \omega t}} = \frac{\tau_0 e^{i\delta}}{\gamma_0 i \omega} = \frac{1}{i \omega} G^* \quad (5.8)$$

According to Eqs 5.6 and 5.8, the complex viscosity can be written as follows (Eq. 5.9):

$$\eta^* = \frac{G''}{\omega} - i \frac{G'}{\omega} = \eta' - i \eta'' \quad (5.9)$$

3.3 Effect of nanoparticle morphology and state of dispersion on the rheological behavior

The dynamic viscosity curves are related to the average shape factor and thus the degree of exfoliation (Marchant and Jayaraman, 2002), because the intrinsic viscosity of such suspensions increases with the average particle shape factor (Luciani et al., 1999). For nanocomposites without intercalation or exfoliation, Lepoittevin et al. (Devalckenaere et al., 2002) and Hoffmann et al. (Hoffmann et al., 2000) observed that the behavior of nanocomposites is similar to that of the matrix, due to the low filler rate.

On the other hand, for intercalated and exfoliated morphology, nanocomposites mainly develop the following particular behavior (U and Yurekli, 2001):

- A transition between quasi-liquid and quasi-solid behavior is observed with a very low charge rate (typically <5%). This transition results in a significant increase in the low frequency module G' .

- The prolonged application of a large deformation causes a significant decrease in the linear viscoelastic module and the destruction of the quasi-solid state of the nanocomposite.

Several authors have explained the change between a quasi-liquid behavior and almost solid by forming a percolation network. The latter can be formed at a low rate of clay, for example, thanks to the strong anisotropy of the particles (Galgali et al., 2001) (Devalckenaere et al., 2002) (Hoffmann et al., 2000) (Solomon et al., 2001; Xu et al., 2005; Meincke et al., 2003; Fornes et al., 2001). Wagener and Reisinger (Wagener and Reisinger, 2003) used the low frequency slope of the evolution of G' with frequency to quantify the state of dispersion of clay leaflets. They observe by image analysis that the degree of dispersion increases with the slope of the low frequency complex viscosity. Galgali et al (Galgali et al., 2001), by creep measurements, showed that at low stress, the nanocomposite exhibits a Newtonian behavior with a very high viscosity. As the stress increases, the viscosity drops rapidly, on the order of two decades in a very narrow stress range, which characterizes a threshold fluid behavior (Barnes, 1999).

By applying a large deformation in dynamic mode, Krishnamoorti and Giannelis (Krishnamoorti and Giannelis, 1997) and Ren et al. (Ren et al., 2003) observed a significant decrease in moduli (mainly of G'), which can be attributed to the orientation of the sheets in the flow direction. However, the typical experiment in this field is to apply to the material, initially at rest, a deformation rate for a certain time and to measure the corresponding evolution of the stress (flow “go”). The deformation is then stopped and, after a determined rest period, the experiment is repeated, but in the opposite direction (“return” flow).

Solomon et al. (Solomon et al., 2001) thus demonstrated on polypropylene/MMT nanocomposites an overshoot stress before stabilization. The magnitude of this overshoot is, for the “return” flow, a function of the rest time imposed between the two flows, the load ratio and the rate of deformation. On the other hand, the peak of stress always occurs for the same value of the deformation, close to 1. The authors attribute the existence of this peak of stress to the orientation of the leaflets and the rupture of the initial network structure. At rest, the “reconstruction” of this structure is not due to the Brownian movement, but rather to an attraction between the clay sheets.

Lee and Han (Lee and Han, 2003) also observed stress peaks during start-ups with polycarbonate/organophilic clay nanocomposites. According to the authors, these peaks are attributed to the presence of strong interactions (hydrogen bonds) between the polycarbonate and the surfactants present on the surface of the clay. Lele et al. (Lele et al., 2002) studied the orientation of nanocomposites under flow using in situ X-ray diffraction. After stopping the flow, they observe a rapid decrease in orientation, which remains identical after 1000 s. They suggest that this rapid decay is due to the coupling between the polymer chains and the clay platelets: the relaxation of the matrix would accelerate platelet orientation relaxation.

Through these few examples of the rheological behavior of nanocomposites observed in the literature, it was found that it is extremely sensitive to the structure and the state of dispersion. It can evolve from a very simple behavior, comparable to that of the matrix, to a very complex behavior. The sensitivity of the rheological properties with the structure will make it possible to differentiate the different morphologies that the classical characterization techniques have difficulty in distinguishing, even if there are still many points that are not elucidated on the relationship between the structure and the behavior observed.

3.4 Viscoelasticity of nanocomposites

The goal of rheology is not only to study the viscoelastic properties of fluids but also to model and classify certain families of materials with each other. The manner in which the material flows makes it possible to draw different characteristic curves of the material as shown in Fig. 5.12. Thus, the rheometer achieves discrete stress ramps and measures the shear rate or applies shear rates and measures the resulting shear stress. In both cases, the measurement makes it possible to measure the viscosity at different shear gradients or at different stresses (Ravanagh, 1998).

3.4.1 Newtonian fluids

The rheological behavior of solutions and suspensions depends largely on their concentration and the nature of the material that constitutes them. It can vary from Newtonian behavior to more complex behavior. A solution or suspension is said to be diluted if the particles are sufficiently distant from each other so that the interactions between them can be neglected.

By definition, a Newtonian fluid has a dynamic viscosity independent of the shear rate (“Newtonian curve (perfect viscous)”) as shown in Fig. (5.12A) following Eq. (5.10). In this case, the viscometer alone is sufficient, giving directly a value of viscosity valid whatever are the shear conditions (Ravanagh, 1998).

$$\tau = \eta \cdot \gamma \text{ and } \eta = \frac{\tau}{\gamma} \quad (5.10)$$

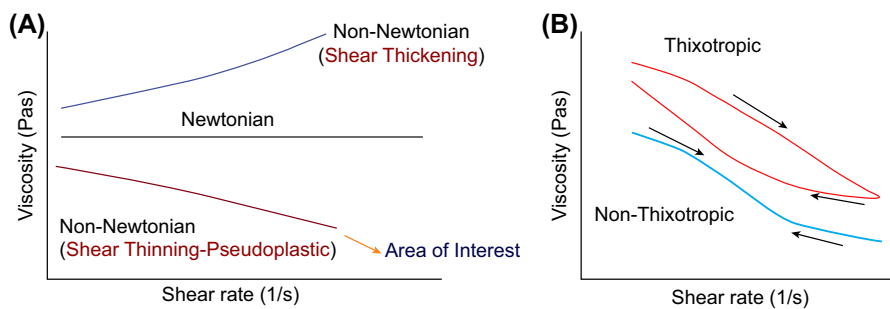


FIGURE 5.12

Different characteristic curves of the material. (A) Non-Newtonian and Newtonian fluids. (B) Nonthixotropic and thixotropic fluids.

3.4.2 Non-Newtonian fluids

Non-Newtonian fluids do not show a linear relationship between shear stress and shear rate. This is due to the complex structure and deformation effects exhibited by the materials involved in such fluids. The non-Newtonian fluids are however diverse and can be characterized as pseudoplastic, dilatants, and thixotropic fluids (Bjrn et al., 2000).

3.4.2.1 Pseudoplastic behavior (shear thinning)

The shearing thinning behavior is the most common; it corresponds to a decrease in viscosity when applying a growing shear rate. For polymer solutions, this behavior is due to the separation of entangled macromolecules and their alignment in the direction of flow as the shear rate increases. In suspensions, the decrease in viscosity comes from the gradual disappearance of organized structures (Ciornei and Alaci, 2015). The shape of the flow curve is shown in Fig. 5.12A. Numerous models have been developed to account for the shear flow of a fluid, giving as many phenomenological models for viscosity.

A much used empirical law for the variation of the viscosity with the velocity gradient is the power law, proposed by Ostwald in 1925 (Eq. 5.11) (Ciornei and Alaci, 2015):

$$\sigma = k \cdot \dot{\gamma}^n \text{ and } \eta = k \cdot \dot{\gamma}^{n-1} \quad (5.11)$$

Where “K” is a coefficient (also called consistency of the fluid) and “n < 1” an exponent which expresses the difference with the Newtonian behavior for which “n = 1” (or index of structure of the fluid). Although this model can solve a large number of flow problems, it should be borne in mind that it does not describe well the low and high shear rate behavior (as we will see later in the last chapter) and that parameters “K” and “n” do not have a clear physical interpretation. In reality, a shear thinning fluid is only for a certain range of shear rates. For low and high shears, Newtonian behavior is observed with the possible appearance of a viscosity plateau. An extension of the power law model is the model of Cross (Eq. 5.12) (Cross, 1965):

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (\lambda \cdot \dot{\gamma})^m} \quad (5.12)$$

Another more sophisticated model than the power law model taking into account zero and infinite shear viscosity trays is the Carreau—Yasuda model (Eq. 5.13):

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = [1 + (\lambda \dot{\gamma})^{\alpha}]^{\frac{m-1}{\alpha}} \quad (5.13)$$

For these two models, η_0 and η_{∞} are, respectively, the zero and infinite shear viscosity, λ is a time constant, and m is a constant and has a parameter which describes the transition between the low shear behavior and the power law.

Another approach is that of Quemada which has the advantage of having a more physical sense than the previous ones. The Quemada model (Baravian et al., 2003)

(Physiologique et al., 1978) was developed to account for viscosity variations in materials containing aggregates rigid, spherical, and noninteractive (concentrated particle suspensions). It is based on the principle of minimal dissipation of energy within the fluid and admits the relation (Eq. 5.14):

$$\eta = \eta_{\infty} \left[\frac{1 + \left(\frac{\sigma}{\sigma_c} \right)^p}{\chi + \left(\frac{\sigma}{\sigma_c} \right)^p} \right]^2 \quad (5.14)$$

Where “ σ ” is the applied stress, “ σ_c ” is the characteristic stress, “ p ” is the slope of the curve at the point of inflection, and “ χ ” is a parameter that depends on the volume fraction $\left(\chi = \frac{\eta_{\infty}}{\eta_0}^{1/2} \right)$.

3.4.2.2 Dilatant behavior (shear thickening)

These are fluids whose viscosity increases with the shear rate. Shear thickening is much more rarely observed than shear thinning. However, some concentrated suspensions (corn starch) and wet sand have a pseudoplastic behavior. A fluid can be dilatant for a certain range of shear rates, and pseudoplastic or even Newtonian for other ranges (Barnes, 1989). The shape of the flow curve is shown in Fig. 5.12A. The shear thickening was first observed by the dilatancy phenomenon evidenced by the Reynolds experiment in 1885. Then, various theories have been developed to explain the phenomenon of shear thickening (Hoffman et al., 1972; Metzner and Whitlock, 1958; Maranzano and Wagner, 2002). Actually, it is believed that the shear thickening is due to the temporary formation of aggregates of particles under shear whose conditions of appearance may differ according to the type of suspensions.

3.4.2.3 Thixotropic behavior

Thixotropic fluids have a viscosity that decreases with time when a constant stress is applied to them. By definition, thixotropy is a reversible variation of the viscosity when a fluid is subjected to a stress (Fig. 5.12B). This assumes that as soon as the applied stress is stopped, the viscosity of the material increases again until it reaches its original value after a certain time. This behavior is interpreted by changes in internal structures of the fluid or even a gradual destruction of this microstructure. This may be similar to a spatial configuration of particles for suspensions or droplets for emulsions, or to an intermingling of macromolecules for polymers. The modification then results from the competition between the hydrodynamic forces (which destroy the microstructure) and the cohesive forces and the Brownian motion (which reform the microstructure) (Barnes, 1997). Examples of everyday life are numerous: food products such as yogurt, cosmetic creams, or even clay suspensions and paints. More rarely, we encounter the opposite behavior, called antithixotropic or rheopectique (Barnes, 1997) (Mewis, 1979), for which the material sees its viscosity increase with time. The modeling of the thixotropic rheological behavior has been the subject of a large number of studies

whose most significant examples are the model of Quemada (Quemada, 1978) (Quemada, 1977), (Quemada, 1978) or Coussot et al (Coussot and Leonov, 1993). This behavior complicates the rheological measurements because hysteresis effects appear.

4. Theory and modeling of nanocomposites rheology

There are several rheological mathematical models applied on rheograms to transform them to information on fluid rheological behavior. For non-Newtonian fluids, the three mostly applied models are presented below (Seyssiecq et al., 2003).

4.1 Herschel Bulkley model

The Herschel Bulkley model is applied to a nonlinear behavior and yield stress fluids. Because its equation has three adjustable parameters, the latter may be considered as a precise model (Seyssiecq et al., 2003). The Herschel Bulkley model is expressed following Eq. (5.15), where τ_0 represents the yield stress.

$$\tau = \tau_0 + k \cdot \gamma^n \quad (5.15)$$

Where (k) is the consistency index parameter which gives an idea of the fluid viscosity. Whereas to compare k values for different fluids, they should have similar flow behavior index (n). When “n” is close to 1, the fluids tend to pass from a shear thinning to a shear thickening fluid. When “n” is above 1, the fluid acts as a shear thickening fluid. According to Seyssiecq and Ferasse (2003), Eq. 4.1 gives fluid behavior information as follows:

$$\tau_0 = 0 \text{ \& } n = 1 \Rightarrow \text{Newtonian behavior}$$

$$\tau_0 > 0 \text{ \& } n = 1 \Rightarrow \text{Bingham plastic behavior}$$

$$\tau_0 = 0 \text{ \& } n < 1 \Rightarrow \text{Pseudoplastic behavior}$$

$$\tau_0 = 0 \text{ \& } n > 1 \Rightarrow \text{Dilatant behavior}$$

4.2 Bingham model

The Bingham model (Eq. 5.16) describes the material flow curve with a yield stress and a constant viscosity at stresses above the yield stress (a pseudo-Newtonian fluid behavior) (Seyssiecq et al., 2003):

$$\tau = \tau_0 + \eta \cdot \gamma \quad (5.16)$$

$$\tau_0 = 0 \Rightarrow \text{Newtonian behavior}$$

$$\tau_0 > 0 \Rightarrow \text{Bingham plastic behavior}$$

Where the yield stress (τ_0) is the shear stress (τ) at shear rate (γ) zero and the viscosity (η) is the slope of the curve at stresses above the yield stress.

5. Conclusion and futures challenges

Nanocomposites are upcoming materials which show the great changes in all the industrial fields. Their use has an enormous benefit as materials. Indeed, they increase in electrical breakdown strength of polymers. Moreover, the interacting zone is increasing such that we can get our expected property. To characterize nanocomposite, the rheology is among the tools the most used. Through the few examples of the rheological behavior of nanocomposites detailed, we find that it is extremely sensitive to the structure as well as the state of dispersion. It can evolve from a very simple behavior, comparable to that of the matrix, to a very complex behavior. The sensitivity of the rheological properties with the structure will help to differentiate the different morphologies that the classical characterization techniques have difficulty in distinguishing, even if there are still many points that are not elucidated on the relationship between the structure and the behavior observed.

The characterization is considered one of the major problems in the area of nanocomposites. As we have shown that the state of dispersion is very sensitive to the rheological behavior, it is interesting to go deeper into this subject to characterize the overall dispersion state of the nanocomposites. The rheological technique proposed in this work makes it possible to study comparatively the effect of the various parameters on the state of dispersion. However, it does not allow precise characterization of intrinsic characteristics, such as particle size and distribution.

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Rheology of polymer-clay nanocomposites

6

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Abstract

The rheological characteristics of various types of polymer-clay nanocomposites along with an overview of various theoretical modeling used are being elaborated here. Different types of polymer-clay nanocomposites with/without organic modification prepared by different methods and under different processing conditions have been discussed.

Keywords: Large amplitude oscillatory shear; Nanofillers; Non-Newtonian behavior; Polymer-clay nanocomposites; Rheology; Small amplitude oscillatory shear.

1. Introduction

The synthesis of polymer nanocomposites by Toyota research group was followed by plethora of studies related to development of nanocomposites for various applications (Toyota, 2014; Kojima et al., 1993). Polymer nanocomposites are materials in which one phase (usually the dispersed phase) is having at least one dimension in the range of nanometers (Karak and Karak, 2012; Huang et al., 2012). The large interfacial area per unit volume of the nano-sized filler provides the nanocomposites' unique properties which make them the best candidate for various applications (Kim et al., 2019; Riehle et al., 2019; Chowdhury et al., 2019) such as transportation vehicles (Paolo et al., 2008), electronic items (Pfaendner, 2010), construction materials (Feldman, 2014), sporting (Shivraj et al., 2016), biomedical industry (Armentano et al., 2010), and various consumer goods (Morgan et al., 2010; Annabi-Bergaya, 2008). Nanoparticles can be divided into three categories (Njuguna et al., 2014):

1. Iso dimensional: all the three dimensions are in nanometer (nm) range.
2. One dimensional: one of the dimensions is in the nm range.
3. Two dimensional: at least two dimensions are in nm range.

Various nanofillers are used quite extensively for improvement in properties leading to the development of smart/advanced materials for various applications (Bai et al., 2019; Yim et al., 2019; Wang et al., 2019; Zimpel et al., 2019). The easy availability and unique intercalation chemistry makes clay one of the most

Table 6.1 Different types of organically modified clays, their trade names, and chemical structure of organic modifier (Lee and Han, 2003).

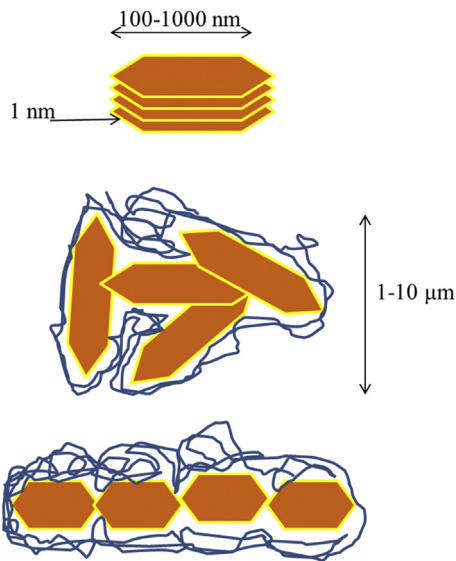
Trade names	Organic modifier	Short name of the modifier
Cloisite 6A	Dimethyl, dihydrogenated tallow, quaternary ammonium chloride	2M2HT
Cloisite 10A	Dimethyl, benzyl, hydrogenated tallow, quaternary ammonium chloride	2MBHT
Cloisite 15A	Dimethyl, dihydrogenated tallow, quaternary ammonium chloride	2M2HT
Cloisite 20A	Dimethyl, dihydrogenated tallow, quaternary ammonium chloride	2M2HT
Cloisite 25A	Dimethyl, dihydrogenated tallow, 2-ethylhexyl quaternary ammonium	2MHTL8
Cloisite 30B	Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride	MT2EtOH
Cloisite 93A	Dimethyl, dihydrogenated tallow, ammonium	M2HT
N28E (Ghanbari et al., 2013)	Octadecyl ammonium	

studied materials (Wilson et al., 2012; Li and Ishida, 2005). Different types of organically modified clays available in the market are given in Table 6.1 (Lee and Han, 2003).

The dispersion of clay in polymer matrix can result in three different situations (Kotsilkova, 2002; Sinha Ray and Okamoto, 2003):

- a.** Tactoids: They consist of layers arranged (stacked) parallel to each other. The shape and director field being determined by a balance of surface anchoring and bulk elastic-free energies. Here the face-to-face interactions predominate, and they usually result in poor mechanical properties (Segad et al., 2012).
- b.** Intercalated: Here the polymer chains diffuse into the intergallery space of the clay layers resulting in an increase in effective volume of the clay. This usually results in edge-to-face interactions, and the nanocomposites usually show an improvement in properties.
- c.** Exfoliated (Delaminated): Here the polymer chains effectively diffuse into the intergallery spacing resulting in a uniform dispersion of the clay layers in polymer matrix. In such a situation, there exist edge-to-edge interaction between the clay layers, and the nanocomposites are expected to have superior mechanical properties. Figure 6.1 shows a schematic representation of the three situations.

The addition of any nanofiller in polymer matrix can result in three different types of interactions namely filler–filler interaction, polymer–polymer interaction, and filler–polymer interactions (James et al., 2014; de Bruyn et al., 2008;

**FIGURE 6.1**

Different situations arising during the mixing of clay with polymer (Lan et al., 1995; Verhoeff et al., 2011; James et al., 2014).

Durán et al., 2000). If the filler–filler/polymer–polymer interaction predominates over filler–polymer interaction, we can expect the formation of tactoids. If filler–polymer interaction predominates over filler–filler/polymer–polymer interactions, it results in exfoliated structure. Thus, it can generally be said that the extent of interaction between filler and polymer decides the extent of its dispersion in polymer matrix (Durán et al., 2000). The extent of interaction depends on clay type, layer charge, pH, etc. (Baghdadi et al., 2005; Paul and Sylvania, 1999). In clay tactoids, the face-to-face interaction predominates, whereas in an intercalated system, edge-to-face interactions exist, and these result in a house of cards structure (Okamoto et al., 2001). In an exfoliated nanocomposite system, edge-to-edge interactions exist. Thus, the rheological behavior of polymer–clay nanocomposites depends on the following factors:

1. The possibility of interaction between polymer and clay.
2. Shear-induced orientation effect.
3. The temperature at which experiment is conducted.

The hydrophilic nature of organoclay and hydrophobic nature of thermoplastic prevents the effective dispersion of clay platelets, making organic modification important in deciding the ultimate properties. Various experimental techniques like wide-angle X-ray scattering (Morgan and Gilman, 2003), transmission electron microscopy (TEM) (Vermogen et al., 2005), diffusion studies (Bousmina, 2006), etc., are widely used to characterize the polymer–clay nanocomposites and to predict

the extent of dispersion of clay in polymer matrix. Rheology is a powerful tool to investigate microstructure and mesoscopic structure of polymer-layered silicate nanocomposites as the low frequency linear viscoelastic response is strongly affected by mesoscopic structure of nanoclay (Wu et al., 2007). Rheological properties are strongly dependent on structure (extent of dispersion of filler/degree of exfoliation in polymer matrix) and interfacial properties, thereby playing a major role in study of polymer nanocomposites. However, detailed investigation of the rheological properties of polymer-clay nanocomposites and application of various theoretical modeling is still limited (Ray, 2013). Main aim of this chapter is to investigate the role of “rheology” in the characterization of polymer-clay nanocomposites under oscillatory shear conditions. A better understanding of the rheological properties of polymer-clay nanocomposites is of extreme importance due to the following:

1. To understand the processability of the nanocomposites (Sinha Ray and Okamoto, 2003).
2. To obtain insights about the structure–property relationships.
3. To investigate the possibility of interactions between nanofiller and polymer matrix.
4. Time-dependent structure development (Mikhail et al., 2005).

1.1 Small amplitude and large amplitude oscillatory shear

Oscillatory shear experiments where stress and strain vary cyclically with time are commonly used in the study of viscoelastic materials (Hyun et al., 2011). Oscillatory shear experiments can be divided into small amplitude oscillatory shear (SAOS) and large amplitude oscillatory shear (LAOS) as shown in Fig. 6.2.

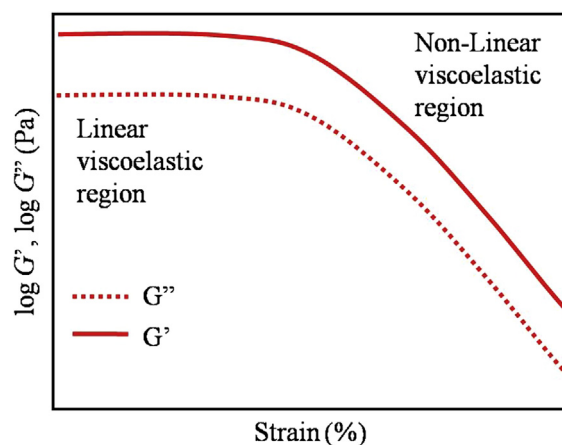


FIGURE 6.2

Different regions/regimes observed in oscillatory shear experiments (Hyun et al., 2011).

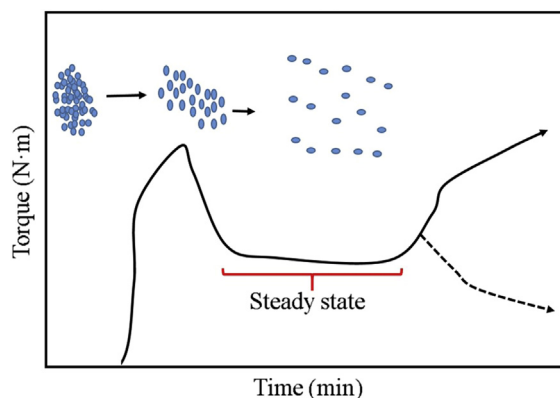
In SAOS, extremely small strain amplitude of the order 10^{-2} to 10^{-1} is applied and the linear viscoelastic regime is considered, whereas in LAOS, large strain amplitudes are applied and nonlinear viscoelastic response is studied in detail (Abhijith, 2009). In SAOS regime, the material functions are not functions of strain amplitude. Material functions obtained from linear viscoelastic region provide information on internal structure and properties (like degree of exfoliation of nanoclay) in polymer blends and nanocomposites (Hyun et al., 2012). Nonlinear response can arise due to large deformations, structural changes, or phase transitions (Malkin, 1995). Rheological response from nonlinear region provides information on topology and morphology of the material. In Fourier transform rheology (FT-rheology), raw stress signal (from LAOS domain) as a function of time is converted into intensity as a function of frequency (Hassanabadi et al., 2014). Nonlinear index (NLI) can be defined as (Morgan and Gilman, 2003)

$$I_{3/1} = \frac{I_{3\omega}}{I_{\omega}} \quad (6.1)$$

NLI is sensitive to microstructural changes of polymer blends and nanocomposites (Salehiyan et al., 2015). Nonlinear viscoelastic ratio (NLR) was used by Salehiyan et al. to quantify the morphology of PP-PS blend system compatibilized using clay and reported that a high NLR value ($NLR > 1$) reflects that organoclay localizes in the dispersed PS phase and interface (Salehiyan et al., 2014). Ock et al. reported the nonlinear viscoelastic response (using FT-rheology) of PLA-NR blends compatibilized with different organically modified clays (Cloisite 10A, Cloisite 20A, Cloisite 30B) (Ock et al., 2016). They reported a decrease in droplet size with (1) increase in mixing rate and (2) increase in compatibilization efficiency (Cloisite 10A > Cloisite 20A > Cloisite 30B). However, no significant change in morphology could be observed. It is noteworthy to mention that the experiments were conducted using PLA (90%)-NR (10%) composition and studies on other compositions can be extremely informative in judging the change in morphology. Rheological properties of semicrystalline polymers are influenced by shear force and crystallization. A competition/collaboration between them and its influence on rheological properties/morphology have not received significant attention (Lei et al., 2016).

2. Effect of clay on mixing torque

The addition of clay in polymer matrix is predominantly reflected in the mixing torque. Atrezi et al. reported the mixing torque as a function of time for ethylene vinyl alcohol (EVA) copolymer modified with organic clay (NANOMER 1.30E) with and without compatibilizer (EVA-g-MA and LLDPE-g-MA) (Artzi et al., 2003). Figure 6.3 shows the variation of mixing torque as a function of time at 230°C and 60 rpm.

**FIGURE 6.3**

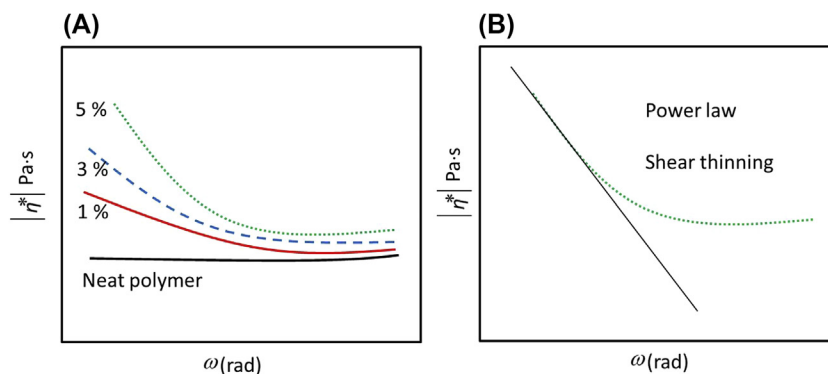
Torque as a function of time for (A) EVA-clay (NANOMER 1.30E) nanocomposite with varying amounts of EVA-g-MA and (B) for LLDPE-clay nanocomposite with varying amounts of LLDPE-g-MA (Artzi et al., 2003).

The increase in torque with addition of EVA-g-MA and LLDPE-g-MA was explained by the fracturing of clay into smaller aggregates along with delamination.

3. Effect of clay addition on complex viscosity

Addition of clay produces a significant alteration in viscosity as shown in Fig. 6.4.

The low shear region is a characteristic of filler, while in high shear region behavior of matrix is predominant. In most cases, the neat polymer exhibits a Newtonian flow at all shear rates; however, addition of clay produces a predominant

**FIGURE 6.4**

(A) Plot of complex viscosity against frequency for neat polymer and polymer-clay nanocomposites, (B) shear thinning exponent calculation using power law model (Gupta et al., 2005).

non-Newtonian behavior with strong shear thinning effect. It can also be observed that the shear viscosity of nanocomposites at high shear rate approaches close to that of neat polymer (refer Fig. 6.4A) (Ray and Okamoto, 2003; Giannelis et al., 1999). Thus, high shear region of Fig. 6.4 shows little change, while the low shear region possesses significant characteristics (Gupta et al., 2005). This has been explained by the fact that intercalated clay layers result in an increase in intergallery spacing which leads to an increase in apparent volume of the tactoids. Thus, intercalation increases the volume content of clay which in turn increases the volume of the polymer nanocomposite. Volume content determines the viscosity and other properties. Thereby,

$$\nu = \nu_0 \frac{l}{l_0} \quad (6.2)$$

Here ν_0 is the initial volume of clay tactoid, ν is the volume of clay after intercalation, while l_0 and l are the interlayer distance of virgin clay and intercalated clay, respectively. The influence of organic modification of clay on the rheological properties of poly(ϵ -caprolactone) was investigated in detail by Lepoittevin et al. using three different types of clay: (1) natural montmorillonite (MMT), (2) MMT modified with dimethyl 2-ethylhexyl (HTA) ammonium (MMT-Alk), and (3) MMT modified with methyl bis (2-hydroxyethyl) ammonium (MMT-(OH)₂) (Lepoittevin et al., 2002). Increasing the amount of MMT-Alk and MMT-(OH)₂ above 1 wt% results in sharp deviation from normal power law behavior indicating a pseudo-solid-like behavior. Choi et al. reported the rheological properties of polyethylene oxide (PEO)-clay nanocomposites using three different types of clay (Choi et al., 2001; Yang et al., 2001). The authors reported an increase in shear viscosity with increase in interaction between organic modifier of clay and polymer due to increase in extent of delamination of clay layers (Sung et al., 2002). However, Ghanbari et al. reported a lower complex viscosity in high frequency region for PET-Cloisite 30B nanocomposites when compared with neat PET, due to matrix degradation which was estimated using Maron–Pierce equation (Ghanbari et al., 2013). The energy required for viscous flow, known as flow activation energy (E_a), can be calculated using Arrhenius equation,

$$\eta = A e^{\frac{E_a}{RT}} \quad (6.3)$$

$$\ln \eta = \ln A + \frac{E_a}{RT} \quad (6.4)$$

Plot of $\ln \eta$ against $1/T$ gives E_a as slope (Akat et al., 2008). Wagener and Reisinger investigated the rheological behavior of poly(butylene terephthalate) (PBT)-clay nanocomposites using SAOS of 1% at 240°C. Shear thinning exponent (n) can be obtained by plotting apparent viscosity (η) against shear rate (ω), as per the power law model (5) (Wagener and Reisinger, 2003),

$$\eta = A \omega^n \quad (6.5)$$

Here A is the sample-specific preexponential factor.

The Newtonian viscosity can be evaluated using Ferry's Eq. (6.6),

$$\frac{1}{\eta} = \frac{1}{\eta_0} + b\tau \quad (6.6)$$

Here τ is the shear stress, while η and η_0 are the viscosities. Wagener and Reisinger concluded that nanocomposites with unmodified clay showed a Newtonian behavior (for very low amounts of clay), while organically modified clay showed strong non-Newtonian behavior (Wagener and Reisinger, 2003). n value decreased from -0.02 to -0.56 and -0.86 as the amount of organically modified clay was increased still, clear/quantitative relation between extent of delamination and shear thinning exponent could not be established (Wagener and Reisinger, 2003). Later, studies by La Mantia et al. on various nanocomposites using Cloisite 15A as nano-filler showed that the value of viscosity (η) and n depends on (La Mantia et al., 2016)

1. Processing conditions.
2. Surface contact area and interaction between the matrix polymer and clay.
3. Degradation of the organic modifier of the clay.

Thus, a general trend or linear change in η and n is not encountered due to variation in the factors discussed above. This also justifies the increase in viscosity and non-Newtonian behavior for organically modified clay systems. The interaction between organic modifier of clay and polymer causes an increase in the volume content of clay. A hysteresis flow curve can be generated by applying a complete cycle of shear, an example of this for polyethylene oxide-Cloisite 25A system is shown in Fig. 6.5 (Yang et al., 2001).

The area enclosed in the hysteresis loop is a measure of the ability of structure recovery of the system under consideration. It can be observed from Fig. 6.5 that

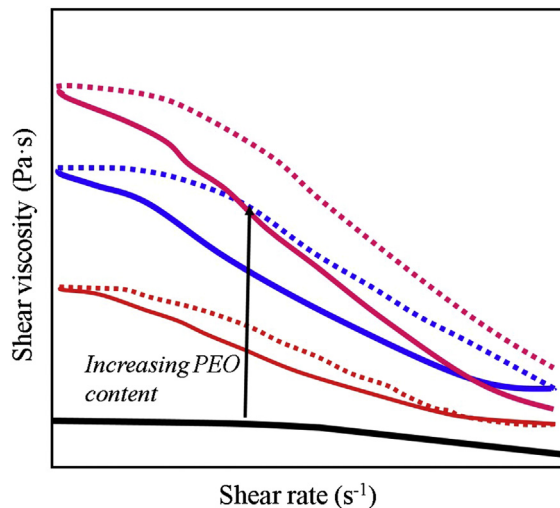


FIGURE 6.5

Schematic representation of hysteresis loop for PEO-Cloisite 25A nanocomposites (Yang et al., 2001).

in the case of neat PEO, a complete recovery of viscosity is observed, while for PEO-Cloisite 25A nanocomposites, equilibrium structure is seldom achieved and the system shows a “fading memory.” The first normal stress difference (N_{12}) defined as $N_{12} = \sigma_{11} - \sigma_{22}$ can be used to measure the melt elasticity of polymeric materials. Krishnamoorthi et al. reported that N_{12} is independent of the amount of clay (Krishnamoorthi et al., 2001). Gupta et al. reported the N_{12} and melt viscosity of EVA-clay nanocomposites and reported that the addition of clay decreases N_{12} at high shear stress (Gupta et al., 2005).

3.1 Reversibility of network formation (effect of hold time)

The effect of experiment time on viscosity of nanocomposites was investigated by Wagener and Reisinger (Wagener and Reisinger, 2003). They reported that frequency sweep experiments conducted soon after one experiment gave low value for viscosity, whereas when the experiment was repeated after a residence time of 1 h, an increase in viscosity was observed. The sharp decrease in viscosity observed for the second experiment was explained by the alignment of clay platelets in the direction of shear, while hold time induces a thermal randomization resulting in an increase in viscosity.

3.2 Effect of particle size and basal spacing

The influence of clay particle size/basal spacing on rheological properties was reported by Moodley (Moodley, 2007). Two organoclays having the same surfactant namely Cloisite 20A (with a particle size of 5 μm) and Dellite 67G (with a particle size of 9 μm) were used to modify PP containing 5% PP-g-MA. In the case of nanocomposites with Cloisite 20A, the basal spacing increased from 2.7 to 3 nm, indicating some degree of intercalation. In the case of Dellite 67G, the basal spacing decreased from 3.7 to 3.4 nm, indicating a collapse of clay gallery.

4. Modeling of viscosity profile

The viscosity profile obtained from rheological studies can be analyzed by different models. In most cases, a Newtonian plateau is observed at low shear rates which then undergo a shear thinning behavior. The shear thinning behavior observed at high shear rates can be due to the alignment of polymer chains and clay layers in the direction of applied shear. This has been discussed in detail in earlier sections. Various theoretical models are available to investigate the viscosity profile.

1. Power law model

It is a two parameter empirical model proposed by Ostwald and de Waele (Gooch, 2007) and has a general form

$$\eta = A\omega^n \quad (6.7)$$

where $A = A_0 e^{\left[\frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]}$

Table 6.2 Flow index (n) and preexponential factor (A) for BIMS modified with different types of clay (Maiti et al., 2004).

Sample composition	Flow index (n)	Preexponential factor (A)
BIMS	0.12	75
BIMS+4wt% of unmodified clay	0.13	64
BIMS+4wt% of organically modified clay	0.09	86

Maiti et al. reported the rheological properties of brominated poly(isobutylene-co-para-methyl styrene) (BIMS) with different clay systems (Maiti et al., 2004). Novolac type phenolic resin was used as the curing agent. The reported values for A and n are shown in Table 6.2, and it was concluded that the addition of unmodified clay results in a decrease in viscosity due to diluent effect, while the addition of organically modified clay increases the viscosity especially at the low shear rate region. Very similar result was reported by Hwang et al. for ethyl vinyl acetate (EVA) modified with MMT in the presence and absence of EVA-g-MA (Huang et al., 2001).

The power law model fails to predict the upper and lower Newtonian plateaus in the limit of zero and infinite shear rates.

2. Herschel–Bulkley model

Herschel–Bulkley equation is given by

$$\sigma = \sigma_y + k\dot{\gamma}^n \quad (6.8)$$

And the viscosity can be calculated as

$$\eta = \tau_0/\dot{\gamma} + k\dot{\gamma}^{n-1} \quad (6.9)$$

Here σ is the shear stress, σ_y is the yield stress, k is a constant, and n is the flow index. $n > 1$ indicates shear thickening behavior, while $n = 1$ points to Bingham plastic behavior, and $n < 1$ shows shear thinning behavior. When $\tau_0 = 0$, Eq. (6.8) reduces to power law model. n , k , and τ are related to the extent of clay dispersion (Gareche et al., 2011). Xia and Song reported the viscosity profile of polyurethane-clay nanocomposites (Xia and Song, 2006). Four different clays, unmodified clay, Cloisite 15A, Cloisite 20A, Cloisite 25A, and Cloisite 30B, were used. Nanocomposites were prepared by dispersing clay in polyol followed by the addition of diol, methyl diisocyanate, and Dabco-33LV. The viscosity profile was very similar to Fig. 6.4A, and a rapid increase in viscosity was observed for Cloisite 30B-based nanocomposites which was explained by the exfoliation/delamination of Cloisite 30B layers due to better interaction with polyurethane matrix (Xia and Song, 2006). Ghanbari et al. reported a modified form of Herschel–Bulkley model to calculate the apparent yield stress (Ghanbari et al., 2013) of poly(ethylene

terephthalate) (PET) nanocomposites with different clays—Cloisite 15A, Cloisite 25A, Cloisite 30B, and N28E.

$$\eta^* = G^*/\omega + k(\gamma^\circ\omega)^{n-1} \quad (6.10)$$

PET-Cloisite 30B nanocomposites gave larger yield stress values indicative of stronger interaction. Ghanbari et al. arranged different clays on the extent of interaction with PET (on the basis of apparent yield stress values) as Cloisite 30B > Cloisite 25A > Cloisite 15A > N28E (Ghanbari et al., 2013).

3. Cross model

To overcome the limitations of power law, Cross presented the following empirical equation (Cross, 1965):

$$\eta = \eta_\alpha + \frac{\eta_0 - \eta_\alpha}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^n} \quad (6.11)$$

Cross equation developed for non-Newtonian fluids is based on the assumption that pseudoplastic flow is connected to the formation and breakage of structural linkages (Tandfonline, n.d.). Cross model is designed to fit the straight line portion between η_0 and η_α . Cross model can be divided into two parts: area including the power law region and infinite shear region called Sisko model and area including zero shear plateau and zero shear region called Williamson model (Ponton et al., 2014). Abdulhadi reported the rheological properties of maleic anhydride-grafted high density polyethylene-Cloisite 15A nanocomposites prepared by melt blending technique using Haake mixer. The viscosity profile showed a better fit with Cross model. The shear thinning exponent (n) and relaxation time showed an increase with Cloisite 15A loading due to increased interaction (Abdulhadi, 2015; Tae, 2002).

4. Ellis model

It is a three parameter model and takes the form (Raju et al., 1993)

$$\eta = \frac{\eta_0}{1 + \left(\frac{\tau}{\tau_{1/2}}\right)^{\alpha-1}} \quad (6.12)$$

Here the non-Newtonian viscosity is a function of the absolute value of shear stress tensor (τ), η_0 is the zero shear viscosity, and α is the slope of $\log\left(\frac{\eta}{\eta_0} - 1\right)$ against $\log\left(\frac{\tau}{\tau_{1/2}}\right)$. In certain cases, the power law fails to recognize zero shear viscosity, and it predicts zero shear viscosity as infinity and infinite shear viscosity as zero (Reddy, 2007). In such cases, Ellis model has found successful applicability. The ratio η_0/τ constitutes a characteristic time of the fluid and is related to fluid elasticity (Chacko et al., 2010; Corcione et al., 2009).

5. Carreau model

Carreau model is a four parameter equation of the form (Hieber and Chiang, 1992)

$$\frac{\eta_{\dot{\gamma}} - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{\left[1 + (\lambda \dot{\gamma})^2\right]^{(1-n)/2}} \quad (6.13)$$

Carreau model can be applied to both low shear rate Newtonian region and high shear rate upper Newtonian region (Mobuchon et al., 2007). Here $\eta_{(\dot{\gamma})}$ is the viscosity at a particular shear rate, η_0 is the zero shear viscosity, and η_{∞} is the infinite shear viscosity. λ characterizes the onset of shear thinning and n is the power law index. The product $\lambda \dot{\gamma}$ reflects the viscoelastic nature of the melt, $\lambda \dot{\gamma} = 0$ for Newtonian fluids. An increase in $\lambda \dot{\gamma}$ indicates decreased viscosity and increased elasticity. Choi et al. reported the relationship between shear viscosity (η) and shear rate ($\dot{\gamma}$) for polyethylene oxide (PEO)-Cloisite 25A nanocomposites using Carreau model (Choi et al., 2001). Accordingly it was reported that the shear thinning behavior, characteristic time, and η_0 increases with increasing clay content, while the critical shear rate ($\dot{\gamma}_c$) (defined as the onset point for shear thinning behavior) decreases. This corresponds to a transformation from liquid like to solid like behavior (Yang et al., 2001). Later, Lim et al. also reported similar results using biodegradable aliphatic polyester (BAPs)-Cloisite 25A nanocomposites (Sung et al., 2002).

5. Carreau–Yasuda (CY) model:

Lertwimolnnum and Verges were the first to introduce CY model for SAOS experiments (Lertwimolnnum and Vergnes, 2006; Han and Jhon, 1986; Pötschke et al., 2002). Nikolic et al. used CY model to quantify the dispersion of Cloisite 15A and Cloisite 30B in poly(ϵ -caprolactone) matrix (Nikolic et al., 2016).

$$\eta = \eta_0 \left[1 + (\lambda \dot{\gamma})^a\right]^{\frac{n-1}{a}} \quad (6.14)$$

where η_0 is the zero shear viscosity, n is the fitting parameter, and a is the Yasuda parameter (Allen, 1999). Yield stress (λ) is a direct indication of the orientation of clay filled nanocomposites and an increase in λ indicate better orientation. Many authors have applied the CY model to PP, PP-g-MA blend system, thermoplastic elastomers, rubber nanocomposites, etc. (Zachariah et al., 2014; Elias et al., 2016; Naderi et al., 2011). Khosrokhavar et al. calculated the yield stress for PP–ethylene-propylene diene monomer (EPDM)-Cloisite 15A (mass fraction-70/20/5) blend nanocomposites prepared by melt mixing using corotating twin screw extruder under different processing conditions. They concluded that an increase in screw speed is accompanied by increase in yield stress indicating an increase in exfoliation of Cloisite 15A layers (Khosrokhavar et al., 2010).

5. Storage modulus (G') and loss modulus (G'')

5.1 Linear and nonlinear viscoelastic properties

Dynamic strain sweep experiments are widely used as the first step to evaluate strain dependence of viscoelastic properties and to calculate the linear viscoelastic region (refer Fig. 6.6A) (Krishnamoorti and Yurekli, 2001). Because G' is more sensitive to structural changes, a plot of G' against strain (%) shows two distinct regions: (1) linear region (Newtonian plateau) at low strain values and (2) nonlinear region at high strain (refer Fig. 6.6A,B). G' value increases with increase in clay content/interaction between clay and polymer chains. However, the transition point (from linear region to nonlinear region) is shifted to low strain values with increase in clay loading/interaction between clay and polymer matrix (refer Fig. 6.6B). The magnitude of transition will be more pronounced for clay and polymer matrix (Durmus et al., 2007; Sangroniz et al., 2016).

Plot of G' versus strain % (refer Fig. 6.6A,B) can be used to obtain critical strain (γ_c). γ_c displays a power law dependency with volume fraction of clay. The slope of $\log \gamma_c$ against $\log v_c$ (volume fraction of clay) provides information on network formation, alignment of clay layers in the direction of strain, and rupture of particle–particle interactions (Jiaxiang, 2000; Wan et al., 2005). In dynamic shear experiments, the application of an oscillatory shear (γ) given by

$$\gamma = \gamma_0 \sin(\omega t) \quad (6.15)$$

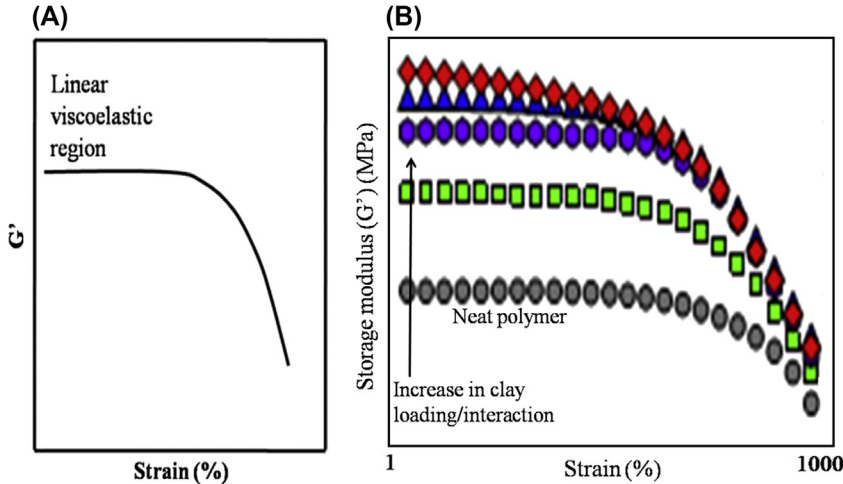
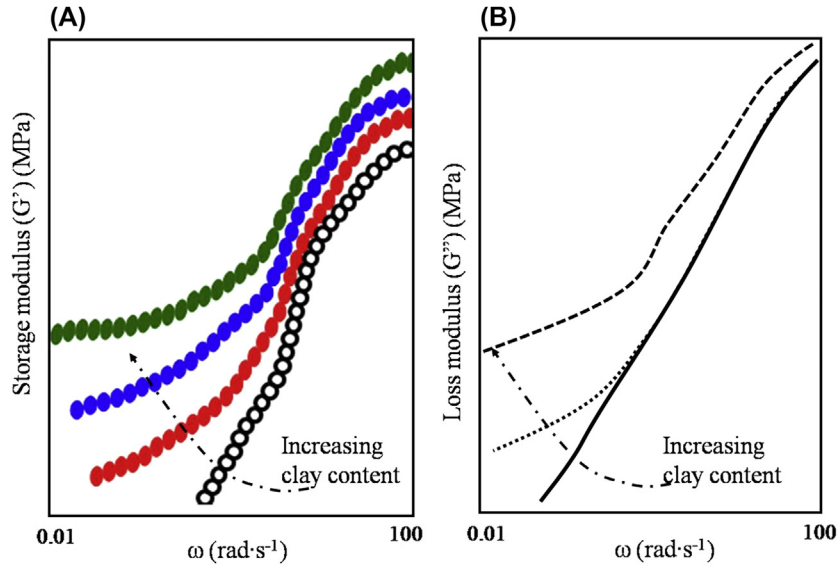


FIGURE 6.6

(A) Variation of storage modulus with strain in dynamic shear experiments, (B) variation of G' as a function of strain (%) for different clay loadings (Wagener and Reisinger, 2003).

**FIGURE 6.7**

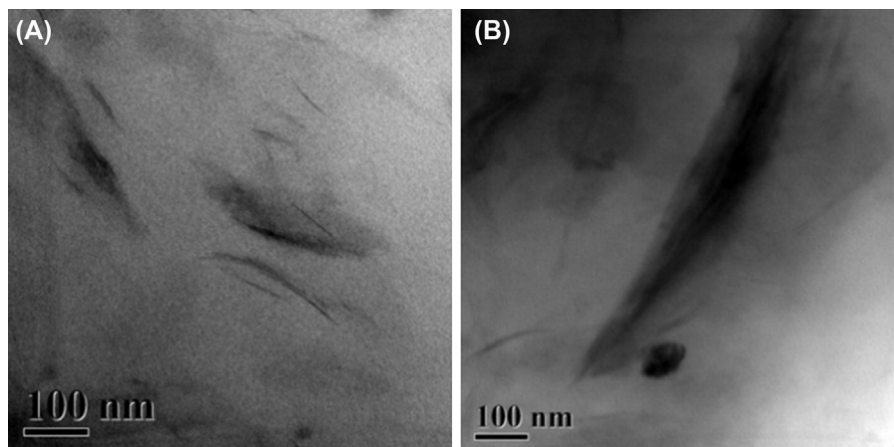
Variation of (A) storage modulus and (B) loss modulus as a function of frequency for different clay loadings (Galgali et al., 2001).

produces a shear stress as

$$\sigma_{(t)} = \gamma_0 (G'_\omega \sin(\omega t) + G''_\omega \cos(\omega t)) \quad (6.16)$$

where G' and G'' are the storage and loss modulus, respectively. In the case of polymer-clay nanocomposites, the high frequency region of G' shows hardly any change, while the low frequency region (in most cases) shows a plateau indicative of a percolated network of clay particles as shown in Fig. 6.7, while a plateau for G'' in the low frequency region is an indication of a gelled system. Thus, G' is more sensitive to structural changes as compared with G'' . Increase in G' in the low frequency region is an indication of strong interaction between clay layers and polymer matrix. The magnitude of increment in G' is an indication of the extent of interaction between clay layer and polymer chains. Durmus et al. reported the frequency sweep results for LLDPE, PE-g-MA, and OxPE using different amounts of Cloisite 20A as the nanofiller (Durmus et al., 2007).

It can be observed that clay loading—dependent change in slope (especially in the low frequency region) is observed which arises due to “pseudo-solid—like behavior.” The soft-concentrated dispersions resulting from “tactoids” produce a change in viscoelastic response at low clay loadings, and the anisotropy of tactoids results in a significant lowering of percolation threshold. According to percolation theory, percolation threshold is defined as the minimum amount of filler required to form a continuous network (Zare, 2017). Fig. 6.8 presents the TEM image of Cloisite 10A dispersed in natural rubber and chlorobutyl rubber (Zachariah et al., 2016).

**FIGURE 6.8**

Exfoliated and intercalated clay layers in (A) natural rubber and (B) chlorobutyl rubber (Zachariah et al., 2016).

Percolation effect is characterized by considerable enhancement in storage and loss modulus coupled with decreased frequency dependence (Favier et al., 1995; Plummer et al., 2005). This rheological behavior arises from strong clay–clay interactions along with large interfacial area between polymer chains and clay (Lim and Park, 2001). Pseudo-solid-like behavior or nonterminal response is an indication of strong clay (filler)–polymer interactions (Krishnamoorti and Giannelis, 1997; Solomon et al., 2001). In the case of neat polymer and nanocomposites with very low clay loadings, $G' \propto \omega^2$ and $G'' \propto \omega$ with a slope of 2 and 1, respectively, are observed as expected for a linear monodispersed polymer system. On increasing the amount of clay, G' , $G'' \propto \omega$ with a slope of one is observed, further increase in the amount of clay results in a more solid-like behavior as shown in Fig. 6.7 (typically noted as nonterminal behavior) (Gu et al., 2004). The concentration at which this transition occurs depends on the extent of dispersion. At higher frequencies, G' and G'' show a power law dependence with frequency. The terminal region of G' and G'' is found to be more sensitive to the amount of clay, and transition from liquid-like to solid-like response is attributed to volume spanning mesoscale organoclay network formation, which hinders the relaxation of clay particles (Galgali et al., 2004; Mitchell and Krishnamoorti, 2002). G'/G'' reflects the melt rigidity associated with reinforcing effect of clay. Ren et al. established that at high clay loadings (beyond percolation threshold) the clay tactoids and individual clay platelets are incapable of free rotation during shearing and cannot completely relax. This incomplete relaxation due to physical jamming beyond percolation threshold leads to nonlinear response (Jiaxiang, 2000). Aghjeh et al. reported the use of SAOS experiments for predicting the localization of clay (Cloisite 30B) in PLA (75%)-EVA (25%) blend nanocomposites (Aghjeh et al., 2016).

6. Time–temperature superposition

According to time–temperature superposition (tTS), time and temperature have equivalent effects on the rheological properties of linear viscoelastic materials or the temperature dependence of relaxation time required for various relaxation processes is the same (van and Palmen, 1998; Markovitz, 1975).

$$G'_{(\omega, T_r)} = \frac{\rho(T) T_r}{\rho(T) T} G'_{(a_T, \omega, T)} \quad (6.17)$$

$$G''_{(\omega, T_r)} = \frac{\rho(T) T_r}{\rho(T) T} G''_{(a_T, \omega, T)} \quad (6.18)$$

where a_T is the ratio of relaxation times at two different temperatures $\lambda_{K(T)} / \lambda_{K(T_r)}$, ρ is the density, and T_r is the reference temperature. tTS is based on Doolittle's free-volume concept and expressed using William Landel and Ferry (WLF) equation (Ferry, 1980; Naya et al., 2013),

$$\eta_o = e[B(v - v_f)/v_f] \quad (6.19)$$

$$\ln \eta = \ln A + B(v - v_f)/v_f \quad (6.20)$$

Considering the free volume (v_f) to be proportional to temperature, we have

$$v_f = v_f(T_r) + \alpha_f(T - T_r) \quad (6.21)$$

This leads to the WLF equation,

$$\log \eta_{o(T)} = \log \eta_{o(T_r)} - [(B/2.3f_g)(T - T_r)/(f_g/\alpha_f) + T - T_r] \quad (6.22)$$

The fractional free volume (f_g) is given by

$$f_g = v_{f(T_r)}/v_{f(T_r)}/v_{f(T_r)} + v_{o(T_r)} \quad (6.23)$$

This gives the WLF equation as

$$\log a_T = -C_1(T - T_r)/C_2 + (T - T_r) \quad (6.24)$$

Here a_T is the shift factor (also known as frequency shift factor), T_r is the reference temperature selected, and C_1 and C_2 are material constants. At high temperatures, WLF equation approaches Arrhenius behavior and $\log a_T$ is given by (López-Paz et al., 2012; Tschoegl et al., 2002)

$$\log a_T = \Delta H/2.3R(1/T - 1/T_r) \quad (6.25)$$

$$\text{and the activation energy } (E_a) = 2.3RC_1^0C_2^0 \quad (6.26)$$

In certain cases, a vertical shift factor (b_T) is also needed to generate a master curve. tTS principle allows to calculate the G' and G'' values at extremely low frequencies (Cifre et al., 2004). Experimental procedure involves carrying out the measurement at different temperatures followed by the application of a shift factor

to generate a master curve. At low clay loadings, a horizontal shift can be enough as long as there is no particular feature in the curves. In the case of high clay loadings, horizontal/vertical shift factors will be required. When the additive produces/induces structural changes, linear viscoelastic data of storage modulus and loss modulus cannot be superimposed thereby master curve cannot be prepared and tTS fails (Qi and Chen, 2008). tTS provides an opportunity to follow the rheological behavior of polymeric materials over a wide range of frequency at different temperatures. According to Cox–Merz rule, $\eta^*_{(\omega)} = \eta(\dot{\gamma})$ holds good for homo polymers and for nanocomposites with very low filler loadings and fails near the percolation threshold (Krishnamoorti and Yurekli, 2001). Failure of Cox–Merz rule is attributed to a combination of the heterogeneous nature of the nanocomposite and difference in structure formation. Zhao et al. reported the viscoelastic response of polystyrene-clay nanocomposites where clay was modified with 1,2-dimethyl-3-n-hexadecyl imidazolium (DMHDI) between a temperature range of 160–260°C with reference temperature (T_{ref}) of 160°C. Figure 6.9 presents an overview of the master curves generated as function clay loading (Zhao et al., 2005) (Fig. 6.9).

Figure 6.9A shows a typical polymer relaxation with $G' \sim \omega^2$ and $G'' \sim \omega$. Increasing the amount of clay changes the slope of terminal frequency region as $G' \sim G'' \sim \omega$ (refer Fig. 6.9B). Fig. 6.9C shows the presence of three distinct regions: (1) high frequency region where rubbery elastic plateau can be observed and response of polymer chains dominate, (2) intermediate frequencies where a dissipative response is observed due to interplay of clay with polymer chains, and (3) low frequency region with a characteristic solid-like response. In Fig. 6.9D,

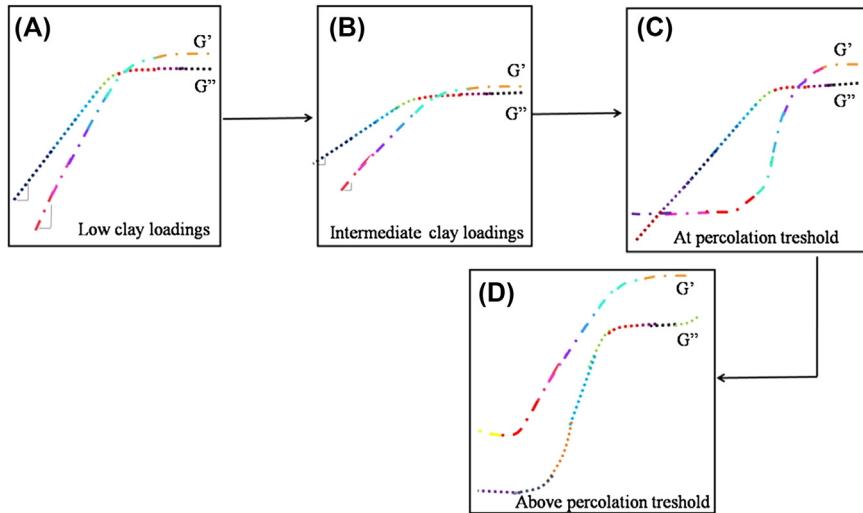


FIGURE 6.9

Schematic representation of time–temperature superposition master curve profile for polymer-clay nanocomposites as a function of clay loading (Zhao et al., 2005).

$G' > G''$ over the entire frequency range. A very similar low-frequency response was reported for polyamide 6-MMT nanocomposites. Mizuno et al. ascribed this to formation of MMT networks with mesoscale dimensions (Mizuno et al., 2013). A qualitative correlation between the extent of clay dispersion and rheological response was confirmed even though a quantitative estimation was not established (Hirota et al., 1999). Hoffmann et al. reported the master curves for polystyrene and polyethylamine (PEA) modified with clay. However, the effect of clay loading, temperature, molecular weight of PS/PEA, etc., were not provided considerable attention (Hoffmann et al., 2000). The effect of adding epoxy resin on viscoelastic properties of polycarbonate-clay nanocomposite was investigated by Wu et al. (Wu et al., 2007). Results similar to that of Fig. 6.7C were reported by Zhong et al. for *in situ* polymerized polystyrene while the addition of 4wt% of MMT (modified with cetyltrimethylammonium bromide (CTAB) and [2-(acryloyloxy)ethyl](4-benzoylbenzyl)dimethyl ammonium bromide (ADAB)). However, a detailed discussion of the slope values and the effect of various surfactants on the viscoelastic response did not receive significant attention (Zhong et al., 2005). Kotsilkova investigated the linear viscoelastic properties of PMMA—organically modified smectic clay nanocomposites prepared by *in situ* polymerization of methyl methacrylate using t-butyl peroxy-2-ethylhexanote (Kotsilkova, 2002). Studies were carried out at different temperatures between 120 and 200°C, and 180°C was selected as the T_r . Krishnamoorti and Giannelis reported the rheology of end-tethered PCL/PA6-clay nanocomposites (Krishnamoorti and Giannelis, 1997). Rheological studies carried out at temperatures between 55 and 160°C, and T_r of 55°C gave a material response very similar to that discussed in Fig. 6.7A–D. Horizontal shifting was enough to generate a master curve for low clay loadings, however, for high clay loadings a vertical shift factor (modulus shift factor) was also required due to nonterminal low frequency response. This nonterminal response was attributed to end tethering of polymer chains which retards the molecular relaxation process. Tethering creates an energy barrier resulting in a dramatic increase in relaxation time. Other notable reasons include (1) undulations and defects in the layers, (2) domain structure of the ordered mesophase, (3) dynamic processes in microscopic and mesoscopic length scales, and (4) topological defects (Krishnamoorti and Giannelis, 1997).

7. Steady shear viscosity

Steady shear rheological parameters such as shear viscosity, shear stress, yield stress, first normal stress difference, etc., provide information about the processability of polymer nanocomposites thereby explaining the structure and orientation/alignment of filler(clay) layers during/after shear (Krishnamoorti et al., 2001; Solomon et al., 2001; Fornes et al., 2001). Gu et al. reported the steady shear viscosity of PP-org-MMT composites mixed with PP-g-MA. Steady shear viscosity shows a monotonic increase with clay loading. Generally, the nanocomposites show a predominant shear thinning behavior, which begins at lower shear rate with increasing

clay loading (Gu et al., 2004). This is due to the alignment of clay platelets in the direction of applied shear.

8. Conclusion

The rheological characteristics of polymer-clay nanocomposites have been subjected to detailed investigation. Rheological parameters (G' , G'' , η , η^*) are strongly dependent on clay loading and clay–polymer interaction. Sharp divergence from terminal behavior to nonterminal behavior can be observed depending on the amount of clay, extent of interaction, and processing parameters. Increase in mixing time and torque produces predominant change in rheological parameters due to enhanced delamination of clay layers. Extent of interaction between clay and polymer matrix can be tailored by increasing the loading of clay/using suitable organic modifier. In certain cases, introduction of functional groups on host polymer can also be helpful. Suitable example for this is the use of maleic anhydride–grafted polypropylene where there is a considerable improvement in delamination of clay layers. In the case of blend nanocomposites, the selective localization of clay can also be followed using rheology. However, limited studies are available on semicrystalline polymer–based blend nanocomposites over different composition range. At low loadings of semicrystalline polymer, confined crystallization and crystal structure can be altered by the amount of clay. Similarly in cocontinuous region, clay loading–dependent change in structure and rheological properties can be observed and these areas require significant attention.

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Rheology of polymer blend nanocomposites

7

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Abstract

A review on the rheological features of polymer blend nanocomposites (PBNANOs) is presented. The role played by nanoparticles to fine-tune the morphology of immiscible blends, substituting conventional compatibilizers, is highlighted. Most of the reviewed papers center their attention on the dynamic (oscillatory) viscoelastic properties in the linear regime, in which the structure of these complex systems remains unaffected. It is seen that the authors have been able to link the linear rheological results to the morphology of PBNANOs and establish viscoelastic models to calculate the interfacial tension between polymer phases. The suitability of the oscillatory techniques, in the linear and nonlinear regime, to detect the coalescence of the droplets of the dispersed polymer phase is presented, even when the works referred to the nonlinear regime are scarce. Regarding to these latter rheological measurements, continuous extrusion flow and extensional flow results on PBNANOs are also reviewed.

Keywords: Dynamic viscoelasticity; Extensional flow; Hybrid materials; Interfacial tension; Morphology; Nanocomposites; Rheology; Shear flow.

1. Definition of polymer blend nanocomposites

Polymer blend nanocomposite (PBNANO) is the name employed in this work to refer to immiscible polymer blends that contain nanoparticles. In literature, different terms have been employed to refer to this kind of systems: filled immiscible blend (Elias et al., 2008; Fenouillot et al., 2009; Liebscher et al., 2018; Scaffaro and Botta, 2014), hybrid ternary blend (Amoabeng et al., 2017; Huang et al., 2014; Huitric et al., 2009; Labaume et al., 2013; Li et al., 2015; Taguet et al., 2014; Ville et al., 2012; Wu et al., 2009), or PBNANO (Ko et al., 2009; Lee et al., 2016; Navas et al., 2017; Nofar et al., 2016; Rostami et al., 2015; Salehiyan et al., 2017; Wang et al., 2017; Yu and Huang, 2015). However, a consensus about the adequate location has not been reached yet and Table 7.1 summarizes the different terms employed, so far.

Table 7.1 Employed terminology in the literature to refer to polymer blend nanocomposite (PBNANO).

Term	References
Filled immiscible blend	5 (Elias et al., 2008; Fenouillot et al., 2009; Liebscher et al., 2018; Scaffaro and Botta, 2014)
Hybrid ternary blends	7 (Amoabeng et al., 2017; Huang et al., 2014; Huitric et al., 2009; Labaume et al., 2013; Li et al., 2015; Taguet et al., 2014; Ville et al., 2012; Wu et al., 2009)
Polymer/nanoparticle system	1 (Taguet et al., 2014)
PBNANO	8 (Ko et al., 2009; Lee et al., 2016; Navas et al., 2017; Nofar et al., 2016; Rostami et al., 2015; Salehiyan et al., 2017; Wang et al., 2017; Yu and Huang, 2015)
Nanofiller compatibilized blends	2 (Salehiyan et al., 2014a, 2014b)
Nanoparticle filled blend	2 (Amoabeng et al., 2017; Kong et al., 2018a, 2018b)

As can be seen, sometimes the term *ternary* (Amoabeng et al., 2017; Huang et al., 2014; Huitric et al., 2009; Labaume et al., 2013; Li et al., 2015; Taguet et al., 2014; Ville et al., 2012; Wu et al., 2009) is employed, but it does not seem to be very adequate, as in some cases, besides nanofillers, compatibilizers or chain extenders are added, so we prefer to employ a more general term (i.e., polymer blends nanocomposites) that encompasses all these systems.

2. Reported PBNANOs in the literature for immiscible blends: relevance of the localization of the nanoparticles

In the literature, different polymer blends have been employed to study the effect of nanoparticle addition. Nanoparticles used include silica in particular (Elias et al., 2007, 2008; Kong et al., 2014, 2018a, 2018b; Li et al., 2015; Liu et al., 2018; Palacios et al., 2016; Salehiyan et al., 2014a, 2015a; Sangroniz et al., 2015, 2016; Vermant et al., 2004, 2008; Wang et al., 2017; Yan et al., 2018; You and Yu, 2018; Yu and Huang, 2015; Zou et al., 2013) and clay nanoparticles (Genoyer et al., 2017; Hong et al., 2006a, 2006b; Huitric et al., 2009; Labaume et al., 2013; Monfared and Jalali-Arani, 2015; Nofar et al., 2016; Ock et al., 2016a, 2016b; Salehiyan et al., 2016; Ville et al., 2012). Less papers report on the use of carbon nanotubes (CNTs) (Gumede et al., 2017, 2018a, 2018b; Ko et al., 2009, 2010; Lee et al., 2016; Urquijo et al., 2017; Wu et al., 2009) and graphene and its derivatives (Bai et al., 2017; Liebscher et al., 2013; Mao et al., 2012).

As it is remarked along this chapter, the presence of nanoparticles affects the morphology of PBNANOs. For most cases, a reduction of the dispersed phase has been reported (Elias et al., 2007, 2008; Genoyer et al., 2017; Huitric et al., 2009; Labaume et al., 2013; Li et al., 2015; Monfared and Jalali-Arani, 2015; Nofar et al., 2016; Ock et al., 2016a; Sahnoune et al., 2017; Salehiyan et al., 2014a, 2015b, 2017; Sangroniz et al., 2015, 2016; Vermant et al., 2004; Ville et al., 2012; Wu et al., 2009), notwithstanding there are a few cases where coarsening has been observed (Gahleitner et al., 2005; Hong et al., 2006a; Kong et al., 2018a; Moghimi et al., 2014; Nagarkar and Velankar, 2012; Salehiyan et al., 2014a). In addition of changing the size of the dispersed phase, the morphology can be varied obtaining co-continuous or different kind of morphologies, as has been reported by Amoabeng et al. (2017). They have systematically studied the effect of varying the polymer blend composition and the content of filler on the final morphology of the blend, observing that new morphologies can be obtained as a result of the presence of nanoparticles.

Most of the works in the literature focus on obtaining a refinement of the dispersed phase, with the aim of replacing the traditional compatibilizers by using nanoparticles. A reduction of the dispersed phase size has been reached for systems in which the nanoparticles locate in the matrix, in the dispersed phase or at the interface. Actually, this location can vary from the beginning of the blending procedure to the final morphology within the solidified material. The mechanisms that take place in the reduction of the size of the dispersed phase are complex because different factors are involved: decrease of the interfacial tension, modification of the viscosities of the polymeric phases (as a result of the presence of fillers), development of a physical barrier around the dispersed phase avoiding coalescence, reduction of the mobility of the droplets or the matrix, due to the creation of a physical network constituted by the nanoparticles, and steric hindrances (Salzano de Luna and Filippone, 2016; Scaffaro and Botta, 2014; Taguet et al., 2014).

In other cases, it has been reported that the location of the filler in the matrix does not alter the morphology (Li et al., 2009; Ock et al., 2016a; Sangroniz et al., 2016), as is the case of polypropylene (PP)/polyamide (PA)/hydrophilic nanosilica PBNANO rich in PP and containing compatibilizer (Sangroniz et al., 2016).

Before summarizing the works reported in literature, the factors that affect the location of the nanoparticles are explained. The final location of nanoparticles in immiscible blends depends on thermodynamic and kinetic aspects (Scaffaro and Botta, 2014; Taguet et al., 2014). Regarding the thermodynamic aspects, the interactions between the nanoparticles and the polymers have to be considered. For that, the wettability parameter is calculated using Young equation, which considers the interfacial tension between the three components (Elias et al., 2007; Fenouillot et al., 2009; Sumita et al., 1991).

Calculations of the wettability parameter are considered to be a good way to predict the location of the nanoparticles; however, in some cases, they do not provide a correct estimation. In fact, it should be considered that thermodynamic equilibrium is not attained. Because of the high melt viscosity of the polymers,

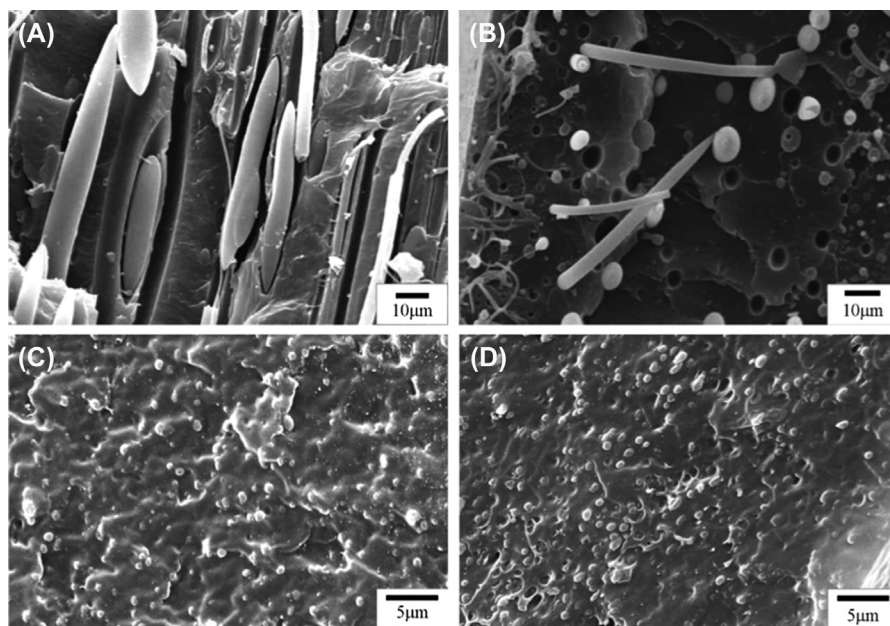
the time needed to reach the equilibrium state is longer than that employed in the mixing or processing of the materials. Therefore, kinetic aspects should be considered, which include the mixing sequence used in the processing of the materials and the migration of the nanoparticles from one phase to another (Scaffaro and Botta, 2014; Taguet et al., 2014).

Elias et al. (2007) studied PP 70/polystyrene (PS) 30/nanosilica PBNANOs containing two different kinds of nanosilica. It was observed that hydrophilic nanosilica particles were located inside the PS droplets, whereas hydrophobic nanosilica particles were situated both in the PP matrix and at the interface. Although both nanosilica particles were reported to be quite effective reducing PS droplets size, the hydrophilic nanoparticles were slightly more efficient. These authors studied the effect of changing the mixing sequence, preparing first a PP/hydrophilic silica nanocomposite and then adding it to PS, observing that silica migrated from PP to PS droplets.

PP 80/PA-6 20/nanosilica PBNANOs have also been studied in the literature (Sangroniz et al., 2015). Using hydrophobic nanosilica, a large reduction of droplet size was observed. The particles were located mainly at the interface and inside the PP matrix, and thus the authors explained the size reduction considering that the particles located at the interface act as a physical barrier preventing coalescence. In the case of systems prepared by film extrusion, the binary blends showed fiber-like morphology because of orientation during flow, as is observed in Fig. 7.1. Notwithstanding, the blends containing nanosilica showed a droplet matrix (i.e., sea-island) morphology and the size of the dispersed droplets was similar to that of compression molded samples. This reflects the efficiency of nanosilica in stabilizing the morphology and therefore in avoiding coalescence and the production of fibers.

A PP/PA 80/20 blend containing a compatibilizer and two different kinds of nanosilica has also been studied (Sangroniz et al., 2016). The compatibilizer led to a strong reduction of the droplet size, from 10 to 0.8 μm (volume average diameter). This reduction was even greater when hydrophobic nanosilica was added: these particles were located at the interface and in PP matrix, as can be observed in Fig. 7.2. However, in the case of hydrophilic nanoparticles, these were located inside PA droplets (see Fig. 7.2), and the size of the droplets remained similar to the blend containing only compatibilizer.

Hyun et al. studied PP/PS/nanosilica PBNANOs employing hydrophobic and hydrophilic nanosilica particles (Salehiyan et al., 2015a). The analysis of the morphology revealed that only the hydrophobic nanoparticles reduced the size of the dispersed phase. On the contrary, the hydrophilic particles led to larger droplets and fibrils at high concentrations. Transmission electron microscope (TEM) images disclosed that the hydrophilic nanoparticles are located inside the PS droplets (Fig. 7.3); thus the viscosity of the droplets increased, making their breakup more difficult. Regarding the hydrophobic nanosilica, the most efficient one reducing the droplet size, termed D17 (modified with dimethyl dichlorosilane), is located at the interface, and thus a barrier is formed which avoids coalescence of

**FIGURE 7.1**

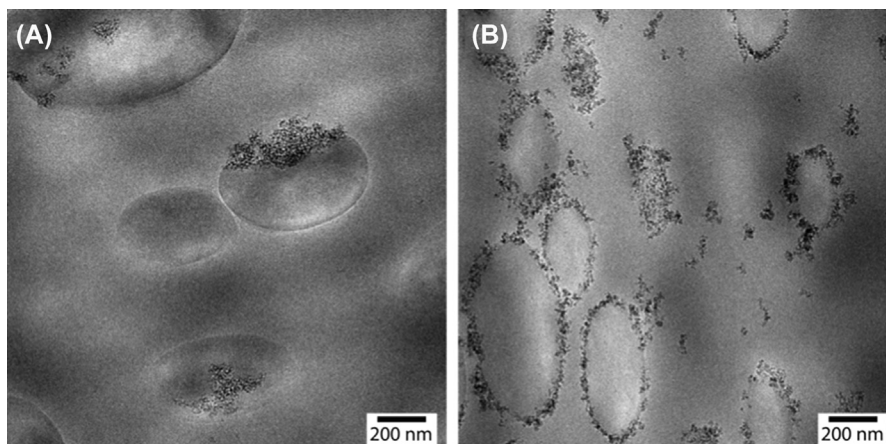
Scanning electron microscope images of PP/PA blends prepared by film extrusion: at the top the binary blend (A) in the machine direction, (B) in the transversal direction. At the bottom, PP/PA/nanosilica polymer blend nanocomposite (A) in the machine direction and (B) in the transversal direction.

Reprinted with permission from Sangroniz, L., Moncerrate, M.A., De Amicis, V.A., Palacios, J.K., Fernández, M., Santamaria, A., Sánchez, J.J., Laoutid, F., Dubois, P., Müller, A.J., 2015. The outstanding ability of nanosilica to stabilize dispersions of Nylon 6 droplets in a polypropylene matrix. *J. Polym. Sci. B Polym. Phys.* 53 (22), 1567–1579. Copyright (2015) Wiley.

the droplets. The other hydrophobic nanoparticle (R202 modified with poly(dimethylsiloxane)) is located inside the PP matrix and in this case the reduction of the dispersed phase size is attributed to the increase of the viscosity matrix, which hinders the film drainage.

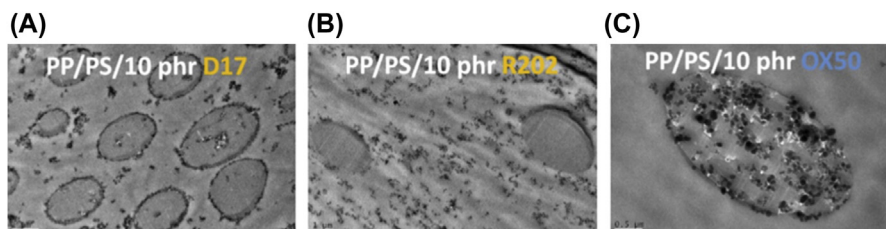
The same research group studied also PP/PS/Cloisite PBNANOs (Salehiyan et al., 2016). In agreement with the results obtained for the blend with nanosilica, the hydrophobic nanoparticles were more efficient reducing droplet size. TEM images revealed that the hydrophobic nanoparticles located at the interface, whereas hydrophilic ones were situated inside the PS phase.

On the other hand, PBNANOs containing CNTs have been studied in literature. Sundararaj et al. studied PS/PA/CNT PBNANOs observing that the nanoparticles were always located inside the PA phase, even though PA was the matrix in one of the blends and the dispersed phase in the other (Hoseini et al., 2017). When PA was the matrix, the viscosity increased because of the presence of CNTs, which

**FIGURE 7.2**

Transmission electron microscope images of PP/PPgMA/PA/NS polymer blend nanocomposite: (A) hydrophilic nanosilica located inside PA droplets; (B) hydrophobic nanosilica located at the interface and in the PP matrix.

Reprinted with permission from Sangroniz, L., Palacios, J.K., Fernández, M., Eguiazabal, J.I., Santamaria, A., Müller, A.J., 2016. Linear and non-linear rheological behavior of polypropylene/polyamide blends modified with a compatibilizer agent and nanosilica and its relationship with the morphology. *Eur. Polym. J.* 83, 10–21. Copyright (2016) Elsevier.

**FIGURE 7.3**

D17 nanosilica is mainly located at the interface, with few particles in the matrix, whereas R202 is located in the matrix: Both are hydrophobic nanoparticles. On the right, the hydrophilic nanoparticles (OX50) are seen located inside PS droplets.

Reprinted (adapted) with permission from Salehiyan, R., Song, H.Y., Choi, W.J., Hyun, K., 2015a. Characterization of effects of silica nanoparticles on (80/20) PP/PS blends via nonlinear rheological properties from fourier Transform rheology. *Macromolecules* 48 (13), 4669–4679. Copyright (2015) American Chemical Society.

resulted in a higher breakup of PS droplets. On the other hand, when PA was forming the dispersed phase, the viscosity of the droplets increased, hindering coalescence, which resulted in a significant refinement of droplets in comparison with the neat blend. However, increasing CNT concentration increased the droplet size of PA because droplet breakup was more difficult.

In the case of polyethylene terephthalate (PET)/low-density polyethylene (LDPE)/multiwalled carbon nanotube (MWCNT) PBNANOs, McNally et al. observed that the nanoparticles tended to locate inside the PET phase, although increasing the content of MWCNTs some of the nanoparticles located inside the LDPE phase (Cardinaud and McNally, 2013). For the PET 20/LDPE 80 blend composition, a reduction in PET droplet size was observed as MWCNTs were added. It has been reported that the presence of nanoparticles can change the morphology of the blend from sea-island to co-continuous (Ko et al., 2010). In fact, Amoaabeng et al. (2017) showed that for polyisobutylene (PIB)/polyethylene oxide (PEO)/silica PBNANOs, the presence of particles led to new kinds of morphologies, with respect to the binary blend. These authors studied deeply PIB/PEO blends with different compositions, analyzing the effect of silica particles, which showed more affinity with PEO, at concentrations up to 30% (Huang et al., 2016). It was observed that the presence of particles facilitated the formation of co-continuous morphologies.

Macosko et al. have deeply studied co-continuous morphologies (Bai et al., 2017; Huang et al., 2016; Trifkovic et al., 2015). They found that for LDPE 45/PEO 55 blends, the addition of silica nanoparticles led to a co-continuous morphology (Huang et al., 2016). LDPE/silica nanocomposites were prepared in a first step and then PEO was added. Hydrophilic silica nanoparticles tend to locate inside the PEO phase, whereas hydrophobic ones were placed at the interface. Annealing the blends led to coarsening, but the addition of low concentrations of hydrophobic nanosilica suppressed coarsening. PLA/PS 48/52 blend, which contained r-GO particles, was also studied by Bai et al. (2017). The role played by the mixing sequence was demonstrated: To locate r-GO at the interface, first PLA/r-GO nanocomposite had to be prepared and then mixed with PS; otherwise, r-GO nanoparticles shifted to the PS phase. The presence of r-GO at the interface prevented coarsening effectively. Interestingly enough, the selective location of r-GO nanoparticles at the interface led to a really low conductivity percolation threshold: 0.028% in volume.

The effect of nanoparticles on phase separation has been also studied in the literature (Vleminckx et al., 2011; Xavier et al., 2014). For instance, Vleminckx et al. (2011) studied the effect of thermally reduced graphene on the phase separation of miscible poly[(alpha-methyl styrene)-co-(acrylonitrile)] (P α MSAN)/poly(methyl-methacrylate) (PMMA) blends. The nanoparticles were located in the P α MSAN phase and it was observed that for P α MSAN contents higher than 40%, the nanoparticles promoted the phase separation of the system.

Nevertheless, in other cases, it has been observed that nanoparticles improve miscibility. Xavier et al. (2014) studied PS/poly[vinyl(methyl ether)] (PVME) 60/40 blends. They observed that the addition of 0.25 wt% r-GO nanoparticles, which were located in the more polar PVME phase, improved the miscibility of the blend.

3. SAOS results reported for PBNANOs and their relationship with interfacial tension and morphology

The most important dynamic viscoelastic functions, that is, the elastic modulus G' , the viscous modulus G'' , and the complex viscosity η^* , in the linear viscoelastic regime, have been widely studied in the literature for PBNANO systems. The advantage of this technique, termed SAOS (small amplitude oscillatory shear), is that as the measurements are performed in the linear regime, the morphology should not change during the measurements, so the viscoelastic parameters can be related with the structure of the material.

Most of the works deal with blends that have droplet-matrix (or sea-island) morphology, although there are some works that study co-continuous blends. The different possible scenarios of the location of the particles in droplet-matrix morphology blends are discussed according to the rheological properties. As explained above, depending on the thermodynamic and kinetic aspects, particles can be located within the matrix, within the dispersed droplet, or at the interface (Scaffaro and Botta, 2014; Taguet et al., 2014). Actually, this is an ideal classification because usually when particles are preferentially located at the interface, some of them can be found in one of the polymeric phases. It should be considered that G' , G'' , and η^* are greatly affected by the size of the droplets, the dispersion degree, and the location of the nanoparticles. As an example, smaller droplets led to higher interfacial area, increasing the elastic component and thus the elastic modulus and the viscosity (Sangroniz et al., 2016).

Considering that modification (i.e., functionalization) of nanoparticles can lead to changes in their final location, several works have been carried out employing SAOS to study the corresponding PBNANOs. When the particles are located in the matrix, G' tends to be higher than when they are located inside the dispersed phase (Genoyer et al., 2017; Monfared and Jalali-Arani, 2015; Salehiyan et al., 2015a; Sangroniz et al., 2016). Above the percolation threshold, the elastic modulus shows a leveling off at low frequencies, which is due to the percolated network formed by particle–particle and particle–polymer chain interactions (Pötschke et al., 2004).

Alternatively, when the filler is located inside the dispersed phase, different behaviors are observed in the literature, although in all cases G' is lower than in the same system with the particles located within the matrix (Genoyer et al., 2017; Monfared and Jalali-Arani, 2015; Salehiyan et al., 2015a; Sangroniz et al., 2016). For some systems, a plateau is observed at low frequencies, in particular when dispersed droplets contain relatively large amounts of nanofillers and have a very high viscosity, acting as a solid (Sangroniz et al., 2016). In other cases, a shoulder is observed (Huitric et al., 2009; Li et al., 2015; Salehiyan et al., 2015a) because the presence of fillers shifts to lower frequencies (longer times) the shoulder which corresponds to the shape relaxation of the droplets. The differences between having a plateau or a shoulder in G' at low frequencies are difficult to correlate with different

morphologies because they could arise from the concentration of the nanoparticles inside the droplets and also from the amount of droplets in the matrix (i.e., the blend composition).

Several works studying the effect of nanosilica in immiscible blends have been reported in the literature (Elias et al., 2007, 2008; Huang et al., 2016; Kong et al., 2014, 2018a, 2018b; Li et al., 2015; Liu et al., 2018; Maani and Carreau, 2016; Nagarkar and Velankar, 2012, 2013; Salehiyan et al., 2014a, 2015a; Sangroniz et al., 2015, 2016; Vermant et al., 2004, 2008; Yan et al., 2018; Yu and Huang, 2015; Zou et al., 2013). One of the first works dealing with immiscible polymer blends containing nanoparticles was that carried out by Vermant et al. (2004). Polydimethyl siloxane (PDMS)/PIB/nanosilica PBNANOs with 70/30 and 30/70 blend compositions were studied with different contents of nanosilica (0.1–1 wt %). Morphological analysis revealed that the nanoparticles were located at the interphase, but some of them could be found in the polymeric phases, being more particles in the PDMS phase. SAOS measurements showed that for 70 PDMS/30 PIB blend, there is a shoulder at intermediate frequencies in the G' versus frequency plot, which corresponds to the form relaxation of the droplet. The presence of silica shifted slightly the shoulder to higher frequencies, i.e., to shorter relaxation times. Different mixing sequences were studied by the authors, but the morphology and thus the rheological properties did not change.

PP80/PS20/nanosilica PBNANOs containing three different silica nanoparticles (1–10 phr) were studied by Salehiyan et al. (2015a). Two nanosilica particles were hydrophobic and the third one hydrophilic. SAOS results revealed that the hydrophilic silica (termed OX50) did not change significantly the rheological properties of the corresponding PBNANOs with respect to PP/PS (80/20) blends because the nanoparticles were located inside the PS droplets, as can be seen in Fig. 7.4A. The observed increase of the elastic modulus was very small, except for the sample with the highest content of filler. In the case of the PBNANO which contained 10 phr nanosilica, a significant G' increase was observed, which was related to a change in the blend morphology because at this silica concentration, a mixture of droplets and fibrils was obtained. The addition of hydrophobic nanosilica increased G' (see Fig. 7.4B and 7.4C), the increase being more significant when the nanoparticles were located inside the PP matrix. The reduction in droplet size was higher in the presence of hydrophobic nanosilica, which was located mainly at the interface (nanosilica D17). Higher G' values were observed for samples in which the nanoparticles were located inside the PP matrix (nanosilica R202) as can be observed in Fig. 7.4C, indicating that the dispersion level and location of the filler prevailed over the droplet size of the dispersed component in the blend.

A blend also based on PP, but containing PA as the dispersed phase (PP/PA 80/20), has been studied in the literature (Sangroniz et al., 2016). The blends were compatibilized with PPgMA and two different types of nanosilica. SAOS data showed that with 5% nanosilica concentration, both nanosilica particles presented a solid-like behavior, according to G' versus frequency results. The G' values were

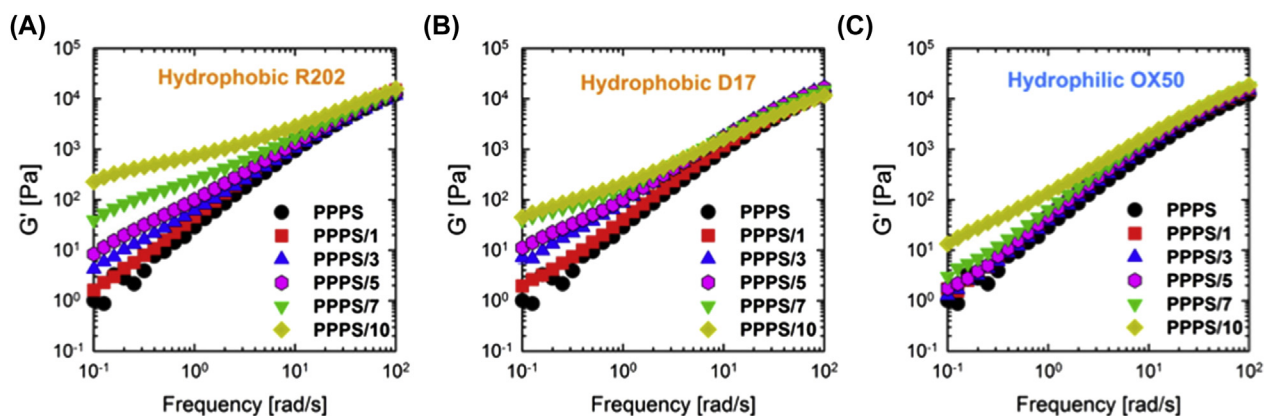


FIGURE 7.4

Elastic modulus obtained by SAOS for PP/PS 80/20 blends containing different nanosilica particles. The different increment of G' for each polymer blend nanocomposite is related to the location of the nanoparticles (see text).

Reprinted (adapted) with permission from Salehiyan, R., Song, H.Y., Choi, W.J., Hyun, K., 2015a. Characterization of effects of silica nanoparticles on (80/20) PP/PS blends via nonlinear rheological properties from fourier Transform rheology. *Macromolecules* 48 (13), 4669–4679. Copyright (2015) American Chemical Society.

higher for the hydrophobic nanosilica, which was located in the matrix and interface: as the silica engulfed the PA droplets, the dispersed phase acted rather as a solid leading to an increase of G' . On the contrary, hydrophilic nanosilica particles were located inside the PA droplets, which led to lower G' values.

Several works have been carried out studying the effect of adding nanoclay to immiscible polymer blends (Chomat et al., 2014; Eslami and Kamal, 2013; Gahleitner et al., 2005; Genoyer et al., 2017; Hong et al., 2006a, 2006b; Huang et al., 2014; Huitric et al., 2009; Kelnar et al., 2015; Labaume et al., 2013; Monfared and Jalali-Arani, 2015; Nofar et al., 2016; Ock et al., 2016a, 2016b; Salehiyan and Hyun, 2013; Salehiyan et al., 2014a, 2014b, 2015a, 2016, 2017; Ville et al., 2012). In the case of 80/20 and 20/80 polyethylene (PE)/PA blends containing clay nanoparticles (1–6 wt%), the rheological measurements showed that the critical strain at which the linear regime ends was reduced with clay addition (Huitric et al., 2009; Labaume et al., 2013; Ville et al., 2012). Complex viscosity η^* increased with clay addition for PE/PA 80/20 blends (i.e., with a PE matrix). As can be seen in Fig. 7.5, in the case of the corresponding PBNANO which contained 4% nanoclay, located at the interface, the plot of the complex viscosity against frequency showed two plateaus, at low and intermediate frequencies, respectively. The observed plateau at intermediate frequencies was allegedly due to the relaxation of the interphase. For PBNANOs based on PA majority blends (PE/PA 20/80) with nanoclay particles located mostly in the matrix, both plateau regions disappeared for high nanoclay concentrations and an upturn of the viscosity

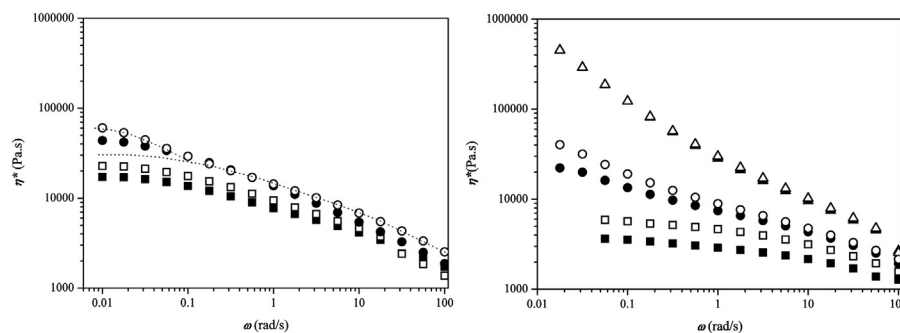


FIGURE 7.5

Complex viscosity as a function of frequency for PE/PA blends containing nanoclay particles. In the left the polymer blend nanocomposite based on PE/PA 80/20 blend: closed squares: binary blend, open squares: 1% clay, closed circles: 2% clay, open circles: 2% clay, and in the right, the blend polymer blend nanocomposite based on PE/PA 20/80: closed squares: binary blend, open squares: 1% clay, closed circles: 2% clay, open circles: 4% clay, closed triangles: 5% clay and open triangles: 6% clay.

Reprinted (adapted) with permission from Huitric, J., Ville, J., Médéric, P., Moan, M., Aubry, T., 2009. Rheological, morphological and structural properties of PE/PA/nanoclay ternary blends: effect of clay weight fraction. *J. Rheol.* 53, 1101–1119. Copyright (2009) American Chemical Society.

at low frequencies was observed, denoting what is commonly known as a yield behavior.

Ock et al. (2016a) studied PLA/rubber/nanoclay PBNANOs, which contain 3 phr of different nanoclays. They observed that when the nanoclay particles were located in the matrix, the value of the elastic modulus G' did not actually change. However, a large increase of G' , accompanied by a solid-like behavior and a droplet size reduction, was observed when the respective nanofillers were located at the interface.

Another group of works in the literature deal with conductive nanoparticles such as CNTs (Cardinaud and McNally, 2013; Ko et al., 2009, 2010; Lee et al., 2016; Liebscher et al., 2018; Rostami et al., 2015; Urquijo et al., 2017; Wu et al., 2009; Zonder et al., 2011) or graphene (Bai et al., 2017; Kurusu et al., 2018; Mao et al., 2012). The presence of CNTs in PLA/PCL blends has been reported in the literature. In particular, PCL 70/PLA 30 blend, which showed droplet-matrix morphology, was studied (Wu et al., 2009). Chemically modified MWCNTs were added to this blend, observing that they were located in the PCL matrix and also at the interface. The binary blend exhibited a shoulder because of the shape relaxation of the droplets and the presence of 0.2 wt% MWCNTs shifted the shoulder to lower frequencies, i.e., longer relaxation times. Also, a reduction of the droplets size was observed, which was compatible with the shift of the shape relaxation associated to an interfacial tension decrease. At higher MWCNT concentrations (0.5–2 wt%), the corresponding storage moduli showed a plateau at low frequencies, indicating that a percolated network was formed. The so-called van Gorp-Palmen-plots (Booij and Palmen, 1982, 1992; Mavridis and Shroff, 1992), $\tan \delta = G''/G'$ versus complex modulus $G^* = G' + iG''$, revealed that the binary blend and the PBNANO with the lowest CNT content (0.2 wt) showed a liquid-like behavior, as the loss factor $\tan \delta = G''/G'$ tended to 90° at low frequencies. However, when 0.5% MWCNT was added, the nanocomposite showed a viscoelastic solid-like behavior ($\tan \delta$ decreased to 45°) indicating rheological percolation. It was concluded that because of the selective location of the CNTs, the rheological percolation threshold was lower for the PBNANO than for the corresponding nanocomposites obtained with each homopolymer.

A few works dealing with the rheological properties of PBNANOs containing Janus particles have been reported in the literature (Caro et al., 2017; Parpaite et al., 2016; Wang et al., 2017). Wang et al. (2017) have studied poly(vinylidene fluoride) (PVDF)/poly(L-lactide) (PLLA) blends containing, respectively, silica, PLLA-grafted silica, and Janus PLLA/PMMA-grafted silica. Janus nanoparticles are particles whose two respective surfaces have distinct physical properties. Silica and PLLA-grafted silica are located inside the PLLA matrix, whereas the Janus particles were situated at the interface. The rheological results showed that only blends containing Janus particles displayed solid-like behavior, see Fig. 7.6A–H. In the case of the other PBNANO, a behavior similar to that of the neat blend was exhibited; in all cases the concentration was 1 wt% and all the blends showed droplet-matrix morphology at 50/50 composition. Van Gorp Palmen plots

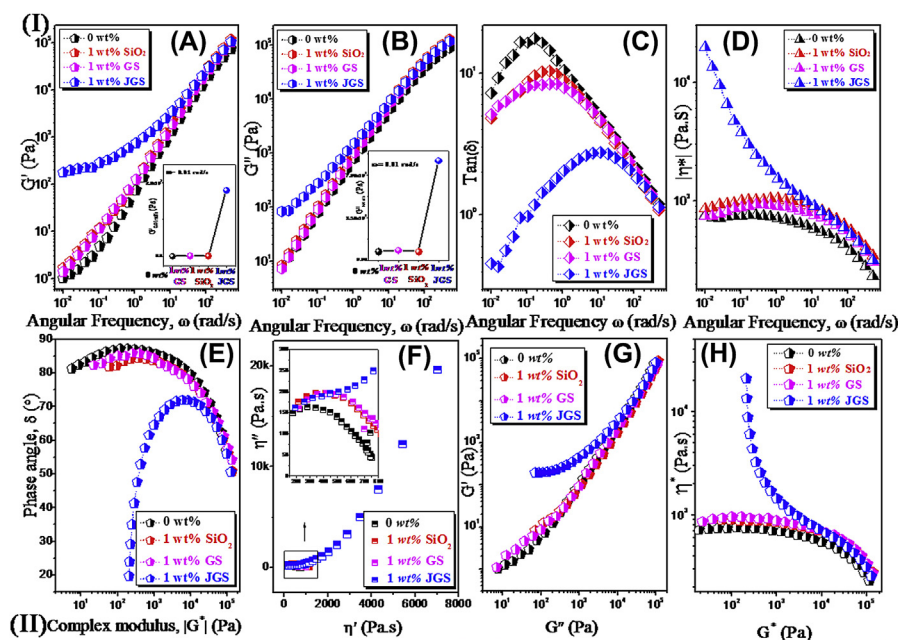


FIGURE 7.6

Rheological properties for PVDF/PLLA containing silica, PLLA-grafted silica, or Janus particles.

Reprinted (adapted) with permission from Wang, H., Yang, X., Fu, Z., Zhao, X., Li, Y., Li, J., 2017. Rheology of nanosilica-compatible immiscible polymer blends: formation of a “heterogeneous network” facilitated by interfacially anchored hybrid nanosilica. *Macromolecules* 50 (23), 9494–9506. Copyright (2017) American Chemical Society.

(Booij and Palmen, 1982, 1992; Mavridis and Shroff, 1992) showed that δ tended to 90° for the binary blend and the PBNANO which contains silica and PLLA-grafted silica, whereas δ decreased for the PBNANO containing Janus particles. Cole–Cole plots (Cole and Cole, 1941), that is to say plots of the imaginary part η'' of the complex viscosity against the real part η' , revealed a tail at long relaxation times for the PBNANO with Janus particles, Fig. 7.6F. Additionally, deviations from the behavior observed for the neat blend and the other nanocomposites in Han plots ($\log G'$ vs. $\log G'$) were reported, see Fig. 7.6G. The authors attributed this conduct to the formation of a heterogeneous network based on interactions between polymer–particle and particle–particle interactions.

Blends having co-continuous morphology and filled with nanoparticles have been scarcely studied in the literature (Bai et al., 2017; Huang et al., 2016; Ko et al., 2010; Trifkovic et al., 2015; Urquijo et al., 2017). However, Macosko et al. have studied several systems in the last years, including PLA/PS/r-GO (reduced GO) PBNANO (Bai et al., 2017). The authors proved that when PLA/r-GO nanocomposite was

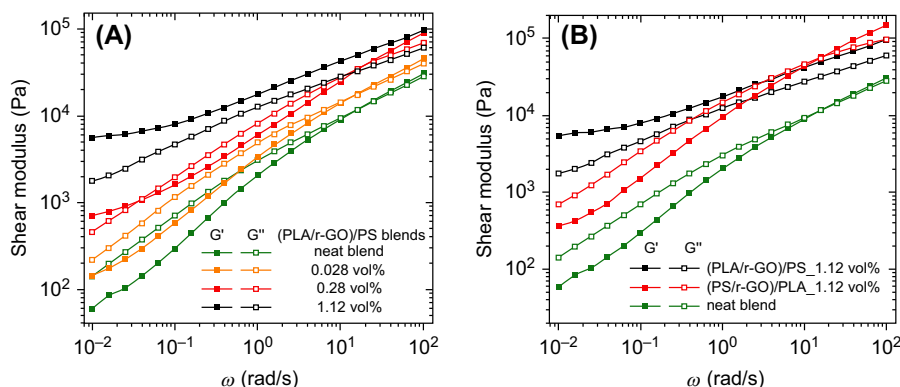


FIGURE 7.7

Elastic modulus against frequency for different PLA/PS/r-GO polymer blend nanocomposites and neat blend.

Reprinted (adapted) with permission from Bai, L., He, S., Fruehwirth, J.W., Stein, A., Macosko, C.W., Cheng, X., 2017. Localizing graphene at the interface of cocontinuous polymer blends: morphology, rheology, and conductivity of cocontinuous conductive polymer composites. *J. Rheol.* 61 (4), 575-587. Copyright (2017) American Chemical Society.

blended with PS to obtain the corresponding PBNANO, r-GO nanoparticles tended to migrate to the polymer interface. The rheological measurements revealed that the neat blend showed a liquid-like behavior, but when the added amount of r-GO was above the percolation threshold, G' dominated over G'' , as can be observed in Fig. 7.7. This gel-like behavior was the result of the r-GO network constituted at the interface path.

Taking advantage of SAOS results, the interfacial tension of immiscible blends can be obtained. Paliarne proposed a constitutive equation for immiscible polymer blends based on equations for emulsions (Graebling et al., 1993; Paliarne, 1990). The model (see Eqs. 7.1-7.2) was developed in the linear viscoelastic regime; therefore, it considers that the deformation of the droplets is small. This means that the size of the droplets is constant and that the effects of breakup and coalescence are not considered.

$$G^*(\omega) = G_m^* \frac{1 + 3 \sum_i \phi_i H_i(\omega, R_i)}{1 - 2 \sum_i \phi_i H_i(\omega, R_i)} \quad (7.1)$$

$$H_i(\omega) = \frac{4 \frac{\alpha}{R_i} [2G_m^*(\omega) + 5G_d^*(\omega)] + [G_d^*(\omega) - G_m^*(\omega)] [16G_m^*(\omega) + 19G_d^*(\omega)]}{40 \frac{\alpha}{R_i} [G_m^*(\omega) + G_d^*(\omega)] + [2G_d^*(\omega) + 3G_m^*(\omega)] [16G_m^*(\omega) + 19G_d^*(\omega)]} \quad (7.2)$$

where G_m^* is the complex shear modulus of the matrix, G_d^* is the complex shear modulus of the dispersed phase, ϕ_i is the volume fraction of the dispersed phase, α is the interfacial tension, and R_i is the radius of the inclusions.

This model predicts an elastic modulus curve with two plateaus that correspond, respectively, to the entanglements network elasticity and to the droplets deformation elasticity. The plateau observed at low/intermediate frequencies is related to the time λ required for a deformed droplet to recover its spherical equilibrium, which can be calculated as follows:

$$\lambda_1 = \frac{R\eta_m}{4\alpha} \frac{(19K + 16)(2K + 3 - 2\phi(K - 1))}{10(K + 1) - 2\phi(5K + 2)} \quad (7.3)$$

where R is the radius of the droplets, η_m is the viscosity of the matrix, α is the interfacial tension, K is the viscosity ratio, and ϕ is the volume fraction of the dispersed phase.

[Elias et al. \(2007\)](#) studied PBNANO systems based on PP 70/PS 30 blends containing 3 wt% hydrophilic and hydrophobic nanosilica to detect the shape relaxation of the droplets. To apply the Palierne model, they fitted their G' and G'' data and made different assumptions regarding the location of the nanoparticles, which affects the viscosity ratio K . In the case of hydrophilic silica, it was considered that the nanoparticles were located inside PS droplets and thus the interfacial tension was reduced from 2.15 for the blend to 0.085 mN/m for the PBNANO; this caused a reduction of PS droplet size. On the other hand, hydrophobic silica nanoparticles were observed to be located in the PP matrix and the interfacial tension was not reduced. The authors concluded that the mechanism of the reduction of the droplet size is the silica layer surrounding PS droplets, which act as a solid barrier avoiding coalescence.

In the case of PBNANO systems based on PP 80/ethylene vinyl acetate (EVA) 20 blends with hydrophilic and hydrophobic nanosilica (3 wt%), which always were located in the EVA phase, the shape relaxation of the droplets in PBNANO was not distinguished from the relaxation of the blend ([Elias et al., 2008](#)). To overcome this issue, it was considered that the complex moduli of the blend were composed by the complex moduli obtained without considering the interface and the droplet complex modulus G_d^* , which corresponds to the interfacial effect $G_{Palierne}^* = G_{composition}^* + G_{droplet}^*$. Therefore, obtaining the size of the droplets by scanning electron microscope measurements, they were able to fit the experimental data to the model and estimate the interfacial tension. The authors obtained a value of 0.75 mN/m for the PP 80/EVA 20 binary blend, which was reduced to 0.25 mN/m in the case of PBNANO.

Instead of applying Palierne model to the experimental data, [Vermant et al. \(2004\)](#) subtracted the contribution of the components using a linear mixing rule in the study of PDMS/PIB blends. Therefore, they analyzed only the contribution of the interface; they applied [Eq. \(7.3\)](#) and the relaxation time was determined from

the crossover between G' and G'' . The ratio between the interfacial tension and the droplet size was studied with the applied shear rate.

Gramespacher and Meissner (1992) considered that the complex modulus of the blend results from the addition of the complex moduli of the components and the contribution of the interfacial tension:

$$G_{blend}^* = G_{components}^* + G_{interface}^* \quad (7.4)$$

To describe the effect of the interfacial tension on the moduli, they employed a model developed by Choi and Schowalter for concentrated emulsions of two Newtonian liquids, in which interfacial tension is defined as follows:

$$\alpha = \frac{\eta_m R_v}{\tau_0} \frac{(19k + 16)(2k + 3)}{40(k + 1)} \left[1 + \phi \left(\frac{5(19k + 16)}{4(k + 1)(2k + 3)} \right) \right] \quad (7.5)$$

in which

$$k = \frac{\eta_{dispersed \ phase}}{\eta_{matrix}} \quad (7.6)$$

where R is the radius of the dispersed phase and τ_0 is the shape relaxation time.

To obtain the relaxation time τ_0 , the weighted relaxation spectrum has to be plotted $\tau H(\tau)$ versus τ . In the case of blends, sometimes a third peak appears in the spectrum at longest times. This peak is related to the shape relaxation of the droplets and is connected with the interfacial tension.

The Gramespacher and Meissner method was applied by Salehiyan et al. (2014a) to a PBNANO constituted by PP/PS blends filled with clay and silica, observing that it is a valuable technique to estimate the interfacial tension. Notwithstanding, it should be considered that the method was proposed for dilute systems and rather monodisperse size droplets, which is not the usual case in polymer blends. The authors determined the relaxation time τ_0 to be used in Eq. (7.5) from the maximum of the relaxation spectrum. It was reported that the addition of nanofiller shifted the form relaxation of the droplets to longer times. For the PBNANO containing 7 wt% clay, the size of the droplets was reduced and the interfacial tension diminished from 1.9 for the blend to 0.36 mN/m. In the case of the PBNANO which included silica, for low silica concentrations, the size of the droplets was reduced, as well as the interfacial tension. However, at high concentrations (7 wt%), the size of the droplets increased and the interfacial tension rose to 3.16 mN/m.

Hong et al. (2006b) proposed a different method to estimate the interfacial tension for polybutylene terephthalate 10/PE 90 blends, based on extensional rheology experiments. The study of extensional force revealed that the presence of clay reduced the force, which led to assume a reduction of the interfacial tension for PBNANO. The interfacial tension was obtained using the following equation:

$$F_{blend} \approx \phi_1 F_1 + \phi_2 F_2 + \alpha + D \times N_{droplet} \quad (7.7)$$

where ϕ is the volume fraction, F is the extensional force, N_{droplet} is the number of droplets, D is the volume averaged diameter of domain, and α is the interfacial tension. Using this method, it was noted that the interfacial tension was reduced from 5.76 cN/m for the blends to 0.14 cN/m for the PBNANO with 1% of clay. It should be remarked that in some PBNANOs it is not possible to determine the interfacial tension because the concentration of nanoparticles is above the percolation threshold, which hides the form relaxation of the droplets.

4. LAOS results reported for PBNANO

The rheological properties under large amplitude oscillatory shear (LAOS) measurements have been scarcely studied in literature, although from an academic and an applied point of view relevant information can be inferred from nonlinear viscoelastic experiments (Hyun et al., 2011; Wilhelm, 2002). In fact, it should be considered that most processing operations occur in the nonlinear regime.

The dependence of the viscoelastic moduli G' and G'' with the strain amplitude has been reported for a few PBNANOs. It has been observed that the addition of fillers led to a reduction of the critical strain amplitude at which the storage modulus is no longer independent of strain amplitude (Ock et al., 2016a; Salehiyan and Hyun, 2013; Salehiyan et al., 2014a, 2015a, 2016; Sangroniz et al., 2015, 2016). This effect is also known as Payne effect (Payne, 1965). For immiscible polymer blends, it is known that the onset of nonlinearity depends on the deformability of the droplets: the more deformable the droplets are, more severe is the deviation from linearity (Ziegler and Wolf, 1999). In the case of systems containing fillers, including PBNANO, the reduction of critical strain amplitude has been related to the breakup of the network constituted by the nanoparticles or deagglomeration of the clusters (Elias et al., 2008; Salehiyan et al., 2014b, 2015a, 2015b). The increase of the filler content leads to a lower critical strain amplitude, as has been reported for PP/PS filled with silica and organoclays (Salehiyan et al., 2014a, 2015a, 2016) and PLA/poly(butylene succinate) filled with organoclay (Salehiyan et al., 2017).

Salehiyan et al. (2015a) studied PP/PS blends with different silica and different localizations of the nanoparticles. The onset of nonlinearity occurred at lower strain amplitudes for the PBNANO containing hydrophobic nanoparticles. The shortest linear region was observed when the nanoparticles were located at the interface. This also gave rise to smaller droplets, as compared with those of the blends. For PBNANO that contained hydrophobic nanoparticles located inside PS, the deformability of the droplets was logically decreased and the linear region was extended. The studies performed with PP/PA blends containing a compatibilizer and different kind of nanosilica particles revealed that the PBNANO with the smallest droplet size showed the lower critical strain amplitude, but a correlation between the droplet size and the critical strain amplitude could not be established (Sangroniz et al., 2016).

The measurements performed in the nonlinear regime provide qualitative information, but different methods are used to deepen in the analysis of the data obtained by LAOS, such as Lissajous curves and Fourier transform (FT) rheology (Hyun et al., 2011; Wilhelm, 2002). In the case of PBNANOs, most of the works reported in literature deal with FT rheology, but some attempts have been made with Lissajous curves. Fourier transformation converts the time-dependent signal into a frequency-dependent spectrum, representing the intensity of the different harmonics. In general, the third relative harmonic (I_3/I_1) is studied because it is the strongest signal. In literature, it has been proved that this parameter is sensitive to the droplet size and interfacial tension in immiscible emulsions (Hyun et al., 2011). For PBNANO, it has been observed that if the addition of filler reduces the size of the dispersed phase, the intensity of third relative harmonic (I_3/I_1) increases. This behavior is observed in Fig. 7.8 and the I_3/I_1 parameter against the strain amplitude for PP/PA system is shown. A nonlinear parameter known as Q can be calculated with the following equation: $Q = \frac{I_{3/1}(\omega)}{\gamma_0^2}$ (Hyun and Wilhelm, 2009). The Q parameter for PP/PA system is shown in Fig. 7.8. At low-strain amplitudes, Q is constant and the parameter Q_0 , which quantifies the nonlinearity, can be obtained using the equation (Lim et al., 2013):

$$Q = \frac{Q_0}{1 + (C_1 \gamma_0)^{C_2}} \quad (7.8)$$

where C_1 and C_2 are adjustable parameters.

For PP/PA and PP/PS blends, it has been found that there is an inverse relationship between the Q_0 parameter and the size of the droplets (Sangroniz

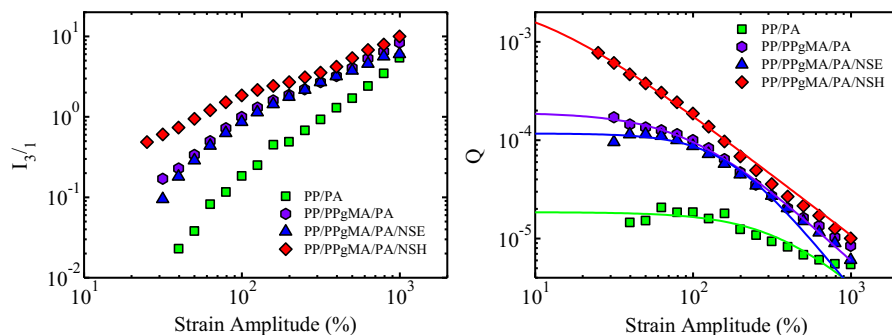


FIGURE 7.8

On the left the intensity of third relative harmonic for the different PP/PA systems. On the right the nonlinear parameter Q for the different PP/PA systems.

Reprinted with permission from Sangroniz, L., Palacios, J.K., Fernández, M., Eguiazabal, J.I., Santamaria, A., Müller, A.J., 2016. Linear and non-linear rheological behavior of polypropylene/polyamide blends modified with a compatibilizer agent and nanosilica and its relationship with the morphology. *Eur. Polym. J.* 83, 10–21.

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et al., 2016). In particular, the following equation has been proposed for PP/PA system:

$$Q_0 = \frac{1.9 \times 10^{-4}}{d_v} \quad (7.9)$$

where d_v is the average diameter in volume.

The advantage of this method is that once the equation is established for one system, the data obtained by LAOS can be used to determine Q_0 to calculate the size of the droplet.

On the other hand, Hyun et al. proposed a parameter that involves SAOS and LAOS measurements known as nonlinear–linear viscoelastic ratio (NLR), which is related to the morphology of the blend (Lim et al., 2013):

$$NLR = \frac{Q_0(\phi)/Q_0(0)}{G^*(\phi)/G^*(0)} \quad (7.10)$$

where the corresponding parameters are defined above. $Q_0(\phi)$ is the Q_0 parameter for each system, $Q_0(0)$ is the Q_0 value for the blend without nanoparticles, $G^*(\phi)$ is the complex modulus of each system, and $G^*(0)$ is the complex modulus of the blend without nanoparticles.

This parameter allows evaluating if the effect of filler addition is more significant in the nonlinear regime ($NLR > 1$) or in the linear one ($NLR < 1$): if the effect is the same on both regimes, NLR is equivalent to 1. It was first introduced by Lim et al. (2013) for PCL/MWCNT polymer nanocomposites, but the authors proved that it was useful to evaluate the morphology of PBNANOs (Ock et al., 2016a; Salehiyan et al., 2014a, 2015a, 2016). In fact, when a filler did not reduce the size of the dispersed phase, constant values of NLR were obtained. However, $NLR > 1$ was obtained when a filler acted as a compatibilizer agent fine-tuning the morphology. The size of the droplets was reduced when filler concentration was increased, which led to an NLR increase.

A deeper study of NLR parameter revealed that it reflects the effect of the morphology and the dispersion level of the filler in the polymer phase (Salehiyan et al., 2015a). In particular, higher NLR values were reported for the blends with larger droplet size. To analyze solely the effect of the morphology of the PBNANO, the NLR value was normalized by the NLR value obtained for matrix/nanoparticles nanocomposite. Given this normalization, the highest NLR value was obtained for the smallest droplet size PBNANO.

For PLA/natural rubber (NR) polymer blends filled with different clays and nanosilica particles, which were located inside the polymers, Ock et al. (2016a) proposed an empirical equation which correlated the NLR parameter with the inverse of the radius of the droplets, as can be observed in Fig. 7.9. However, for the PBNANOs in which nanoparticles were located at the interface, the data did not fit to this equation and another equation was proposed.

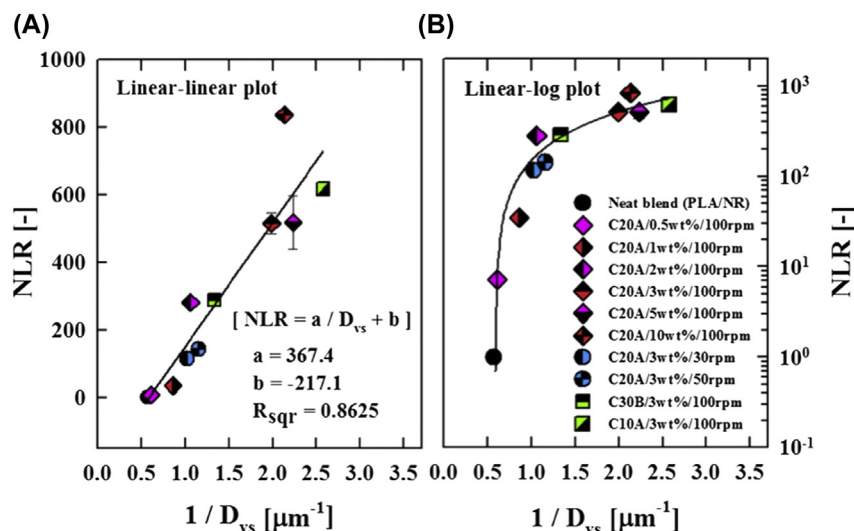


FIGURE 7.9

The values of nonlinear-linear viscoelastic ratio parameter, which is obtained from SAOS and LAOS data (see text), plotted against the inverse of the diameter for PLA/rubber blend containing different types of nanoparticles.

Reprinted (adapted) with permission from Ock, H.G., Ahn, K.H., Lee, S.J., Hyun, K., 2016a. Characterization of compatibilizing effect of organoclay in poly(lactic acid) and natural rubber blends by FT-rheology. *Macromolecules* 49, 2832–2842. Copyright (2016) American Chemical Society.

The authors proved, employing PP/PS/nanoclay PBNANO, that in the medium amplitude oscillatory shear region where Q_0 is determined, the morphology does not vary in comparison with the morphology of the PBNANO before testing (Salehiyan et al., 2016). The size of the droplets only increases at higher strains, which means that Q_0 parameter can be related with the morphology of the PBNANO.

Only in a couple of works, the data obtained from LAOS have been analyzed using Lissajous curves (Salehiyan and Hyun, 2013; Salehiyan et al., 2015b). Usually, the normalized stress (σ/σ_{max}) against the normalized strain (γ/γ_{max}) is plotted, which is known as Lissajous loop. If instead of the strain, the shear rate is used, the plot is called the viscous loop. These kinds of plots give qualitative information about the elasticity of the system. The degree of deviation of the loop with respect to a circular shape (viscous response) accounts for the elastic response of the system (Hyun et al., 2011).

For PP/PS blends (with PS more viscous than PP), Salehiyan et al. (2015b) have observed that the behavior is more elastic (curves more ellipsoidal) at low strains and higher PS concentration. Adding clay to the blends to elaborate PBNANOs led to an increase of the elasticity, as analyzed by Lissajous curves. By increasing the concentration of the filler, a more elastic response was also observed for PLA natural

rubber system (Ock et al., 2016a). Using stress decomposition method (Cho et al., 2005), which decomposes the total stress in the viscous and elastic stresses, it was possible to detect Lissajous curves distortions at large strain amplitudes. However, only some attempts have been carried out for filled polymers and PBNANOs resulting difficult to quantify the nonlinearity, in comparison to FT rheology, although some conclusions regarding the strain hardening can be drawn out (Salehiyan et al., 2015b).

5. Effect of flow on coalescence

In the case of pure binary blends, it has been observed that when high shear rates/stress were applied, there was a reduction of the droplet size, whereas applying low shear rates/stress, coalescence came about (Moghimini et al., 2014; Vermant et al., 2004). The effect of applying shear flow on the morphology of PBNANOs has also been reported in literature, remarking on the effect of the presence of nanoparticles.

The effect of shear flow on PDMS/PIB blends (70/30 and 30/70) was studied by Vermant et al. (2004). They applied shear rates of $0.05\text{--}6\text{ s}^{-1}$ and after cessation of flow SAOS measurements were performed: G' against frequency plots showed a shoulder which was ascribed to the form relaxation of the droplets. The position of the shoulder depends on the applied shear rate because the size of the droplets changes, Fig. 7.10. But it was observed that the addition of silica, to obtain PBNANOs, led to a reduction of this dependency (Fig. 7.10). Given the liaison

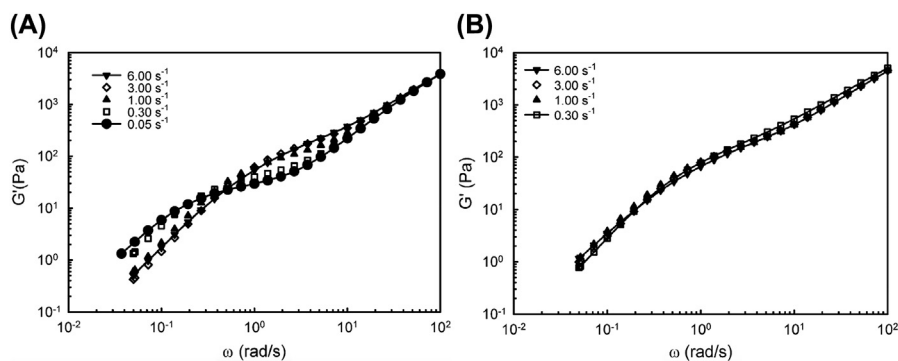


FIGURE 7.10

The elastic modulus as a function of frequency measured after cessation of the respective indicated shear rates (A) PDMS/PIB 70/30 neat blend (B) PDMS/PIB 70/30 1% nanosilica polymer blend nanocomposite.

Reprinted (adapted) with permission from Vermant, J., Cioccolo, G., Golapan Nair, K., Moldenaers, P., 2004. Coalescence suppression in model immiscible polymer blends by nano-sized colloidal particles. *Rheol. Acta* 43 (5), 529–538. Copyright (2004) Rheologica Acta.

between G' and the interfacial tension, as explained above, it can be deduced that for neat blends the ratio of the size of the droplets (R radius) to the interfacial tension α is reduced with shear rate. Vermant et al. observed a reduction of droplet size with the applied shear rate. However, in the case of PDMS/PIB 70/30 1% nanosilica PBNANO, no dependence of R/α on shear rate was inferred.

In the case of polybutadiene (PBD)/PDMS blends (90/10 and 10/90) containing fumed silica (0.1–2 wt%), Zou et al. (2013) observed that the addition of silica reduced the droplet size, but led to the formation of droplet clusters, in particular when shear rate was applied. Shear flow promoted the development of a network, which was noticed by the solid-like behavior ($G' > G''$) observed at low frequencies, especially at the highest silica content. A similar rheological result was obtained by Maani and Carreau, (2016) for PP 75/ethylene octane copolymer (EC) 25/nanosilica PBNANO. Moreover, in this case, a viscosity upturn was also observed at low frequencies.

The effect of different mixing procedures on the morphology of PP 70/PA 30/ organoclay PBNANOs was studied by Huang et al. (2014). Three preparation methods were used: (1) first, PA6/organoclay was mixed and then PP was added, (2) PP/clay was mixed and then PA6 was added, and (3) all the components were mixed at the same time. SAOS measurements showed that both, the binary blend and the PBNANO prepared by the first mixing method (1% clay), had a shoulder which corresponded to the shape relaxation of the droplets. This shoulder shifted to lower frequencies as an increasing shear strain was applied during flow; this was linked to the coalescence of the droplets. For the PBNANOs prepared by the other two methods, no shoulder was detected, allegedly because of the particles location, mostly at the interface, which prevents the deformation of the droplets.

Although, in general, the presence of nanoparticles led to an effective suppression of coalescence, in some cases coalescence was promoted. This was the case of PS/PA6/hydrophilic nanosilica PBNANOs; nanoparticles were located inside the PA6 phase and at the interface, reducing the PA6 droplet size, as compared to neat blend (Kong et al., 2014). However, when a shear strain flow of 0.05 s^{-1} was applied for 4000 s, coalescence was enhanced, as was revealed by the shift to lower frequencies of the G' shoulder. On the contrary, when hydrophobic nanosilica nanoparticles were located inside the PS phase, the morphology was stabilized under the application of a shear flow. Apparently, the reason for this opposite behavior lay on the different viscosities of PA6 and PS phases (Kong et al., 2014).

LAOS measurements have been also employed to study the coalescence in PBNANOs. In the case of PP/PA (80/20) blends compatibilized with PPgMA and nanosilica (5 wt%), LAOS measurements revealed as more sensible than SAOS analysis to study the morphology (Sangroniz et al., 2016). It was seen that the nonlinearity Q_0 parameter, defined above, was significantly reduced as the PA droplet size increased (Fig. 7.11).

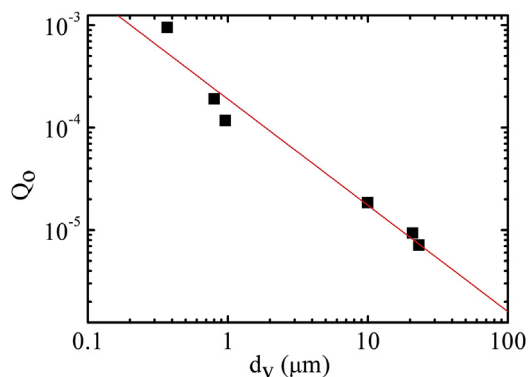


FIGURE 7.11

Q_0 nonlinear parameter for PP/PA blend and corresponding polymer blend nanocomposites against the diameter of the PA droplets (see text).

Reprinted with permission from Sangroniz, L., Palacios, J.K., Fernández, M., Eguiazabal, J.I., Santamaria, A., Müller, A.J., 2016. Linear and non-linear rheological behavior of polypropylene/polyamide blends modified with a compatibilizer agent and nanosilica and its relationship with the morphology. Eur. Polym. J. 83, 10–21.

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6. Other rheological measurement: viscosity as a function of shear rate and extensional viscosity

In the available literature, the viscosity of PBNANOs as a function of shear rate has been scarcely studied, even when this is a relevant issue, as most processing techniques, such as extrusion and injection molding, employ high shear rates.

The influence of MWCNTs on the viscosity of PLA/PBAT/MWCNT PBNANOs was studied by [Ko et al. \(2009, 2010\)](#). According to the authors, the PLA/PBAT 50/50 blend mixed with CNTs showed a more pronounced shear thinning behavior, improving the processability of the PBNANO. This resulted from the alignment of the CNTs in the direction of flow, which contributed to the drastic decrease of the viscosity with shear rate. [Huitric et al. \(2009\)](#) analyzed PET/PA/nanoclay PBNANOs. Neat PE 80/PA 20 blends showed a shear thinning behavior, which was compatible with the observed droplet-matrix morphology. Besides shear thinning, PET/PA/nanoclay PBNANOs displayed also a yield stress, reportedly because of the formation of a percolated network. It is worth pointing out that a yield stress, associated to viscoplastic behavior, can be advantageous for some processing techniques, such as thermoforming in which the sagging of the material should be avoided. Yield stress was also observed in PET/LDPE/TiO₂ PBNANOs, but only with an adequate size of the dispersed LDPE droplets ([Sangroniz et al., 2018a](#)). In fact, by reducing the size of the droplets, the interfacial area was enhanced and therefore the elastic contribution, which led to higher yield stress values.

One relevant issue of multiphase systems, associated to the use of a capillary extrusion rheometer, is the possible morphology changes that occur during flow. In blends with a droplet-matrix morphology, coalescence is more abundant in compression molded samples than in extrudates. But this difference is not practically noticed in the case of PBNANOs.

Extensional viscosity plays an important role in several processing techniques such as blow film extrusion or thermoforming, but, so far, the extensional viscosity of PBNANOs has been scarcely studied. The most relevant feature of the extensional viscosity is strain hardening, i.e., an upturn of the viscosity observed at high strains, which facilitates blow extrusion process. [Eslami and Kamal, \(2013\)](#) studied the extensional viscosity of PLA/poly[(butylene succinate)-*co*-adipate] (PBSA) blends and PLA/PBSA/nanoclay PBNANOs. The extensional viscosity was reported to be higher for PBNANOs than for pure blends, but strain hardening was only observed for the systems rich in PBSA because this polymer showed itself strain hardening. Therefore, the role played by nanoclay particles was not clearly elucidated.

The effect of the location of the nanoparticles on the emergence of strain hardening was revealed by [Ock et al. \(2016b\)](#) in their study of PLA/natural rubber/nanoclay PBNANOs. As can be seen in [Fig. 7.12](#), the sample which contains 2% nanoclay displayed strain hardening, but not the sample with 5%. According to the authors, this was because of the location of the nanoparticles at the interface, which completely covered the interface for 2%, whereas for the PBNANO, which contained 5% nanoclay, the excess of particles was located in the PLA phase. Extensional viscosity results have also been reported for PP/PS/nanosilica ([Kong et al., 2018a](#)). In this study, the effect of the location of the nanofillers on

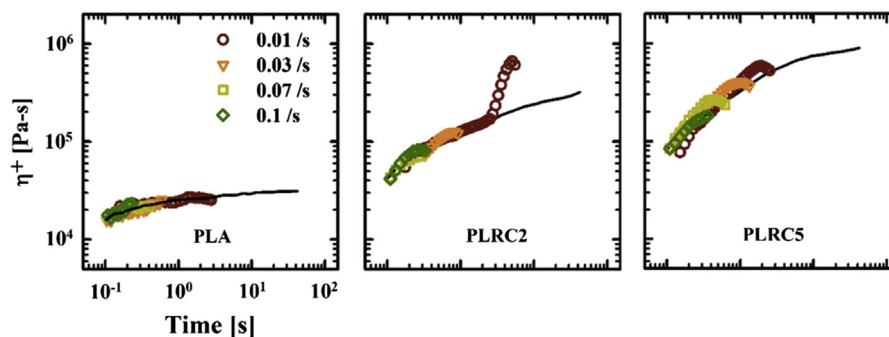


FIGURE 7.12

The extensional viscosity as a function of time at the indicated extensional rates. From right to left: pure PLA; polymer blend nanocomposite (PBNANO) with 2% nanoclay; PBNANO with 5% nanoclay.

Reprinted with permission from Ock, H.G., Kim, D.H., Ahn, K.H., Lee, S.J., Maia, J.M., 2016b. Effect of organoclay as a compatibilizer in poly(lactic acid) and natural rubber blends. Eur. Polym. J. 76, 216-227.

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the extensional viscosity of the PBNANOs was soundly investigated, but strain hardening was not reported.

In literature, the strain hardening behavior has been related to the relaxation time of the system (Kasehagen and Macosko, 1998; Sangroniz et al., 2018b). As the presence of nanoparticles shifts the relaxation time to longer times, a strain hardening behavior could be expected. However, the works reported in the literature show the complexity of these kinds of systems, as the network formation can be broken during extension which avoids strain hardening behavior and on the other hand the presence of nanoparticles at the interface can deteriorate the adhesion between polymer phases.

7. Perspective and future outlook of the field

In the last few years, the study of PBNANOs has attracted great interest. The complexity of these systems is difficult for the understanding of some issues, such as the mechanism of the alteration of the morphology and the variation of the interfacial tension. A comprehensive study of different systems of PBNANOs has allowed the establishment of relationships between the results of SAOS measurements and the morphology of the systems, as well as the location of the nanoparticles. But, as apparently contradictory results are in some cases obtained, more work should be carried out to establish a general scope of the subject.

Regarding the replacement of traditional compatibilizers by nanoparticles, it should be considered that the key factor is the interface, rather than the size of the dispersed phase. Therefore, future research should be focused on the development of nanofillers that, in addition of reducing the dispersed phase, improve the compatibility between the polymeric phases.

A remarkable effort has been done on the correlation between droplet size and rheological parameters, which could be useful in industry, in the aim of using rheological data as a first sight test to characterize PBNANOs. So far, LAOS breaks through as a more feasible method than SAOS to reach this goal. But, new routes should be explored to exploit both, SAOS and LAOS data.

The studies on PBNANOs by other rheological techniques, such as the analysis of the viscosity as a function of shear rate and the research on the extensional flow, are up-to-date clearly insufficient, given its relevance in industrial processing.

An interesting and, so far, practically ignored approach is the development of electrically conductive PBNANOs. The location of the conducting nanoparticles at the interface of co-continuous blends can reduce significantly the quantity of filler required to obtain semiconducting materials, as reported by Bai et al. (2017). Therefore, obtaining polymer systems with a very low electrical percolation threshold in the field of PBNANOs should be achievable and desirable.

Table 7.2 summarizes all the rheological techniques that have been reported in the literature to study PBNANOs.

Table 7.2 Summary of the rheological techniques employed for the polymer blend nanocomposites reported in literature.

Sample	SAOS	LAOS	Extrusion flow	Extensional flow	Others techniques
Silica					
PDMS/PIB/silica Vermant et al. (2004)	Yes				Steady shear viscosity Stress ramp transient creep viscosity
PDMS/PIB/silica Vermant et al. (2008)	Yes				
PEO/PIB/silica Nagarkar and Velankar (2012)	Yes				
PEO/PIB/silica Nagarkar and Velankar (2013)					
PBD/PDMS/silica Zou et al. (2013)	Yes				
PP/PS/Silica Elias et al. (2007)	Yes				Transient shear viscosity
PP/PS/silica and clay Salehiyan et al. (2014a)	Yes	Yes			
PP/PS/silica Salehiyan et al. (2015a)	Yes	Yes			
PP/PS/silica Kong et al. (2018a)	Yes			Yes extensional	
PP/PS/silica Kong et al. (2018b)	Yes				
PP/EVA/silica Elias et al. (2008)	Yes				
PP/PA6/silica Sangroniz et al. (2015)	Yes	Yes			
PP/PA6/silica Sangroniz et al. (2016)	Yes	Yes			
	Yes				

Table 7.2 Summary of the rheological techniques employed for the polymer blend nanocomposites reported in literature.—*cont'd*

Sample	SAOS	LAOS	Extrusion flow	Extensional flow	Others techniques
PP/EC/silica Maani and Carreau (2016)					Transient rheology
PP/PVA/silica Yan et al. (2018)	Yes				
PA6/PS/silica Kong et al. (2014)	Yes				
PC/PMMA/silica Li et al. (2015)	Yes				
PLA/TPU/silica Yu and Huang (2015)	Yes				
LDPE/PEO/silica Huang et al. (2016)	Yes				
SSBR/LPI/silica Liu et al. (2018)	Yes		Yes extrusion		
Clay					
PP/PA6/clay Gahleitner et al. (2005)	Yes		Yes extrusion		Steady shear rheology
PE/PA/clay Huitric et al. (2009)	Yes				
PE/PA/clay Ville et al. (2012)	Yes				
PE/PA/clay Labaume et al. (2013)	Yes				
PP/PA6/clay Chomat et al. (2014)	Yes				
PP/PA6/clay Huang et al. (2014)	Yes				
PP/PS/clay Salehiyan et al. (2014b)	Yes	Yes			
	Yes	Yes			

Continued

Table 7.2 Summary of the rheological techniques employed for the polymer blend nanocomposites reported in literature.—*cont'd*

Sample	SAOS	LAOS	Extrusion flow	Extensional flow	Others techniques
PP/PS/clay and silica Salehiyan et al. (2014a)					
PP/PS/clay Salehiyan et al. (2015b)	Yes	Yes			
PP/PS/clay Salehiyan et al. (2016)	Yes	Yes	Yes extrusion		
PMMA/PS/clay Genoyer et al. (2017)	Yes				
PBT/PE/clay Hong et al. (2006a)	Yes				
PBT/PE/clay Hong et al. (2006b)	Yes			Yes extensional force	
PLA/PBS/clay Eslami and Kamal (2013)	Yes			Yes extensional	
PLA/PBS/clay Salehiyan et al. (2017)	Yes	Yes			
PLA/PCL/clay Salehiyan et al., 2013	Yes	Yes			
PCL/PLA/clay Kelnar et al. (2016)	Yes				
PLA/PBAT/clay Nofar et al. (2016)	Yes				Transient shear viscosity
PLA/NR/clay Ock et al. (2016a)	Yes	Yes			
PLA/NR/clay Ock et al. (2016b)	Yes			Yes extensional	
NBR/SBR/clay Monfared and	Yes				

Table 7.2 Summary of the rheological techniques employed for the polymer blend nanocomposites reported in literature.—*cont'd*

Sample	SAOS	LAOS	Extrusion flow	Extensional flow	Others techniques
Jalali-Arani (2015)					
Conductive nanoparticles					
PLA/PBAT/MWCNT Ko et al. (2009)	Yes		Yes extrusion		
PLA/PBAT/MWCNT Ko et al. (2010)	Yes		Yes extrusion		
PLA/PBAT/CNT Urquijo et al. (2017)	Yes				
PCL/PLA/MWCNT Wu et al. (2009)	Yes				
PLA/PS/r-GO Bai et al. (2017)	Yes				
(PS/PPE)/PA66/CNT Lee et al. (2016)	Yes	Yes			
PMMA/PS/graphene Mao et al. (2012)	Yes				
PA12/HDPE/CNT Zonder et al. (2011)	Yes				
PET/LDPE/MWCNT Cardinaud and McNally (2013)	Yes				
EVA/LLDPE/graphene Kurusu et al., 2018	Yes				
PC/ABS/MWCNT Rostami et al. (2015)	Yes				
PC/SAN/CNTs Liebscher et al. (2018)	Yes				

Continued

Table 7.2 Summary of the rheological techniques employed for the polymer blend nanocomposites reported in literature.—*cont'd*

Sample	SAOS	LAOS	Extrusion flow	Extensional flow	Others techniques
Other nanoparticles					
PS/PA6/Janus nanoparticles Parpaite et al. (2016)	Yes				
PS/PA6/Janus nanoparticles Caro et al. (2017)	Yes				
PS/PA11/halloysite nanotubes Sahnoune et al. (2017)	Yes				
PP/PS/Boehmite alumina Malwela et al. (2018)	Yes				
PVDF/PLLA/Janus nanoparticles Wang et al. (2017)	Yes				
PLLA/PVDF/reactive CNT Zhao et al. (2018)	Yes				
PLA/PC/Janus nanoparticles Yan et al., 2018	Yes				
PET/LDPE/TiO ₂ Sangroniz et al. (2018)	Yes		Yes extrusion		
Study of miscibility/immiscibility					
P α MSAN/PMMA/TRG Vleminckx et al. (2011)	Yes				
PLA/PEO/CNT Zare et al. (2018)	Yes				

List of acronyms and abbreviations

ABS	Acrylonitrile butadiene styrene
CNT	Carbon nanotubes
D17	Hydrophobic nanosilica modified with dimethyldichlorosilane
EC	Ethylene octane copolymer
EVA	Ethylene vinyl acetate
FT	Fourier transform
HDPE	High-density polyethylene
LAOS	Large amplitude oscillatory shear
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
LPI	Low vinyl content polyisoprene
MWCNT	Multiwalled carbon nanotube
NBR	Acrylonitrile butadiene rubber
NLR	Nonlinear—linear viscoelastic ratio
NPs	Nanoparticles
NR	Natural rubber
OX50	Hydrophilic nanosilica modified with methacryloxypropyltrimethoxysilane
PA	Polyamide
PBAT	Poly[(butylene adipate)-co-(butylene terephthalate)]
PBD	Polybutadiene
PBNANO	Polymer blend nanocomposite
PBS	Poly(butylene succinate)
PBSA	Poly[(butylene succinate)- <i>co</i> -adipate]
PBT	Polybutylene terephthalate
PC	Polycarbonate
PCL	Polycaprolactone
PDMS	Polydimethyl siloxane
PE	Polyethylene
PEO	Polyethylene oxide
PET	Polyethylene terephthalate
PIB	Polyisobutylene
PLA	Poly(lactic acid)
PLLA	Poly(L-lactide)
PMMA	Poly(methyl-methacrylate)
PαMSAN	Poly[(alpha-methyl styrene)-co-(acrylonitrile)]
PP	Polypropylene
PPE	Poly(phenylene ether)
PPgMA	Polypropylene-grafted maleic anhydride
PS	Polystyrene
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
PVME	Poly[vinyl(methyl ether)]
R202	Hydrophobic nanosilica modified with poly(dimethylsiloxane)
r-GO	Reduced graphene oxide
SAN	Styrene acrylonitrile

SAOS	Small amplitude oscillatory shear
SBR	Styrene butadiene rubber
SEM	Scanning electron microscope
SSBR	Solution-polymerized styrene-butadiene rubber
TEM	Transmission electron microscope
TiO₂	Titanium dioxide
TPU	Thermoplastic polyurethane
TRG	Thermally reduced graphene

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Rheology of heavy crude oil and asphaltene-polymer composite blends

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Abstract

Polymers have become an integral part of our daily lives with a wide range of applications. Oftentimes, the nature of application demands modifications of properties of polymer composites. Literature survey reveals that asphaltenes (high molecular weight and polar fractions of the crude oil) have been introduced in recent years as a filler to modify the properties of asphaltene-polymer composites. Asphaltenes are often considered as a waste product of petroleum industry but can have implications in strengthening of the polymer composites owing to improved filler–matrix interaction and formation of filler network via reorganization of the particles. In addition, certain polymer blends can improve the flow performance of the crude oil containing asphaltene and/or wax by modifying the rheological properties. This chapter discusses in detail the development in the field of asphaltene-polymer composites and flowability improvement of heavy crude oil using different polymer blends.

Keywords: Asphaltene; Composite; Polymer; Rheology; Thermoplastic.

1. Introduction

Crude oil is a complex mixture of hydrocarbons ranging from lighter and nonpolar to heavy and polar fractions. These fractions can be grouped into four classes, namely saturates, aromatics, resins, and asphaltenes (commonly known as SARA). Heavy oil primarily contains a higher percentage of asphaltenes which are high molecular weight, polynuclear, aromatic species with aliphatic side chains, heteroatoms (such as nitrogen, sulfur, and oxygen), and traces of heavy metals (such as nickel and vanadium). The consistent structure and properties of asphaltene molecules are difficult to define because they represent a solubility class and not a pure component. Asphaltenes increase the viscosity and result in the non-Newtonian behavior of the crude oil.

Polymers have become an integral part of our daily lives with applications such as automotive, food packing, stationery, etc. Often, the nature of application requires the modification of chemical, thermal, and mechanical properties of polymers and that is where the composites come into the picture. Asphaltene is considered as a waste product in the petroleum industry as it causes flowline blockage due to deposition and hurdles in smooth operations of the refinery. Only recently, it has been included in research to consider as fillers for enhancement of desired properties of polymers. Studies on the enhancement of thermal and viscoelastic properties of polymer composites have been carried out using asphaltene as a filler. It was observed that the mechanical and thermal properties of asphaltene-polymer composites increased significantly with the addition of a certain amount of asphaltenes. Polymer blends have been tested in the oil industry for enhancement of rheological properties and flowability of heavy and waxy crude oil as well.

This chapter discusses in details the development in the field of asphaltene-polymer composites and flowability improvement of heavy crude oil using different polymer blends.

2. Properties of heavy crude oil

Crude oil is a complex mixture of hydrocarbons ranging from lighter and nonpolar to heavy and polar fractions. Although there are many classifications on the crude oil type, the most common way to classify the crude oil is based on API gravity as proposed by American Petroleum Institute (API). This helps to define and classify the crude oils which have not been standardized. The API classification for crude oils is mentioned in Table 8.1. The formula for calculation of API gravity from specific gravity is given as below where S.G. is the specific gravity of the crude oil

$$API\ gravity = \frac{141.5}{S.G.\ at\ 60^{\circ}F} - 131.5 \quad (8.1)$$

The values mentioned above are only a rough guideline as the precise difference in API gravity values of light and heavy oil will change depending on the region from where the oil is being produced. The variations as to what are the light and other classifications are dependent on the commodity trading of the crude oil.

There are other definitions of heavy crude oil available in the open literature and among the oil industries. The difference between light and heavy oil (which is

Table 8.1 API classification of crude oil.

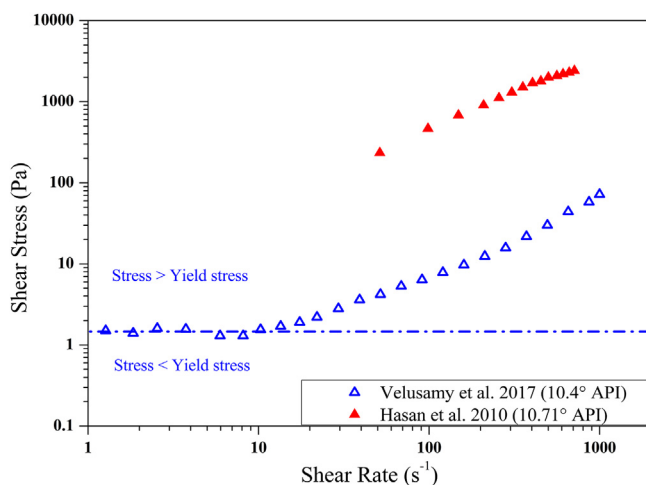
Type	API gravity
Light crude oil	>31.1°
Medium crude oil	22.3–31.1°
Heavy crude oil	10–22.3°
Extra heavy crude oil	<10°

chemically composed of heavy molecular compositions) can be ascribed to the biodegradation process. Over geological timescales, the microorganisms degrade the light and medium hydrocarbons, thus making the reserves rich in poly-aromatic compounds that are asphaltene and resins through oxidation of crude oil and reduction of gas/oil ratio (Head et al., 2003). Heavy crude oils usually have a density almost equal to water, but in some cases, the density might be greater than that of water. They possess different rheological properties and flow characteristics in contrast to the light and medium gravity oil. They are extremely viscous, with a consistency ranging from a heavy liquid to that of a solid at ambient temperature. The complex rheological properties of heavy crude oil create challenges in its upstream production and transportation. Heavy crude oils contain a fairly high amount of higher molecular weight hydrocarbons along with high levels of hetero-compounds (N, S, and O) and metals such as nickel and vanadium. These present a host of problems in refining the petroleum.

2.1 Rheology of heavy crude oil

It is very essential to have a detailed understanding of the rheological properties of crude oils for the design and operation of crude oil transport systems. The rheological properties of a crude oil are highly influenced by its chemical composition. At sufficiently high temperature, most crude oils exhibit Newtonian flow behavior, but when the temperature drops, the agglomeration of polar components such as asphaltene and crystallization of waxes changes its flow behavior to non-Newtonian. Heavy crude oil not only reflects anomalous viscosity but also exhibits viscoelastic properties. The rheological properties of crude oil are generally measured with rotational viscometers. Fig. 8.1 shows a typical flow curve of two different heavy crude oils at 25°C. The heavy crude oil sample with 10.71° API and 995 kg/m³ was obtained from Lloydminster, Canada (Hasan et al., 2010), and the sample with 10.4° API and 997.2 kg/m³ was obtained from Assam, India (Velusamy et al., 2017).

It is evident from Fig. 8.1 that both the heavy crude oils depict non-Newtonian stress—strain relationship. The shear stress increases gradually but significantly with shear rate for the crude oil with 10.4° API, whereas slightly curvy nature is seen in shear stress—shear rate profile for the heavy crude oil with 10.71° API. The heavy crude oil flows at low temperature after attaining a shear stress larger than the yield stress of the crude oil as seen in Fig. 8.1. The viscosity and flow behavior of heavy crude oil are strongly affected by shear rate and temperature. However, the values of shear stress are difficult to measure due to uncertainties, and hence they are less suitable for quantitative analysis (Velusamy et al., 2017). Fig. 8.2 shows the variation in viscosity with temperature, shear stress, and the shear rate for different heavy crude oils. The temperature effect on the viscosity of heavy crude oils (obtained from different oilfields with API gravities below 20° and asphaltene contents ranging from 4.5 wt% to 19 wt%) can be observed from the viscosity—temperature relationship as shown in Fig. 8.2A and viscosity—shear rate relationship in Fig. 8.2B,

**FIGURE 8.1**

Typical flow curve of heavy crude oils measured at 25°C.

Data adapted with permission from Elsevier Hasan, S.W., Ghannam, M.T., Esmail, N., 2010. Heavy crude oil viscosity reduction and rheology for pipeline transportation. *Fuel* 89 (5), 1095–1100. and American Chemical Society Velusamy, S., Sakthivel, S., Sangwai, J.S., 2017. Effects of imidazolium-based ionic liquids on the rheological behavior of heavy crude oil under high-pressure and high-temperature conditions. *Energy Fuels* 31 (8), 8764–8775. Copyright (Elsevier, 2010; American Chemical Society, 2017).

respectively. It is evident from Fig. 8.2B that heavy crude oil exhibits reduced viscosity with an increase in temperature. However, the decrease in viscosity is dependent on the type of the crude oils (composition). On the other hand, it is visible from Fig. 8.2B that the viscosity of the heavy crude oil decreases with an increase in shear rate, thus exhibiting a non-Newtonian behavior. However, they might sometimes exhibit Newtonian behavior across a wide temperature range but viscoelasticity below a certain temperature due to the presence of high molecular weight components rather than low molecular weight paraffins (Ilyin et al., 2016). Fig. 8.2C shows the variation of viscosity with the shear stress for heavy crude oil. The heavy crude oil used in this case had the asphaltene content of 7.5 wt% and API gravity of 15.1°. The viscosity was observed to be nearly constant for the entire shear stress range. More details on the effect of asphaltenes on the rheology of crude oil will be discussed in the subsequent sections. There is a significant difference between the viscosities at different temperatures for both the heavy crude oils (Fig. 8.2B). The shear thinning behavior of heavy crude oil is attributed to the disintegration of its chain like heavy molecules due to the high shear rate. At the high shear rate, the molecules get stretched and orient themselves parallel to the driving force resulting in lower viscosity (Hasan et al., 2010; Al-Roomi et al., 2004). Again, the high molecular weight fractions of heavy crude oil such as asphaltenes, resins, waxes, etc., do not have the chance to agglomerate at high temperature and thereby result in reduced viscosity of the crude oil (Khan, 1996). Some of the important internal

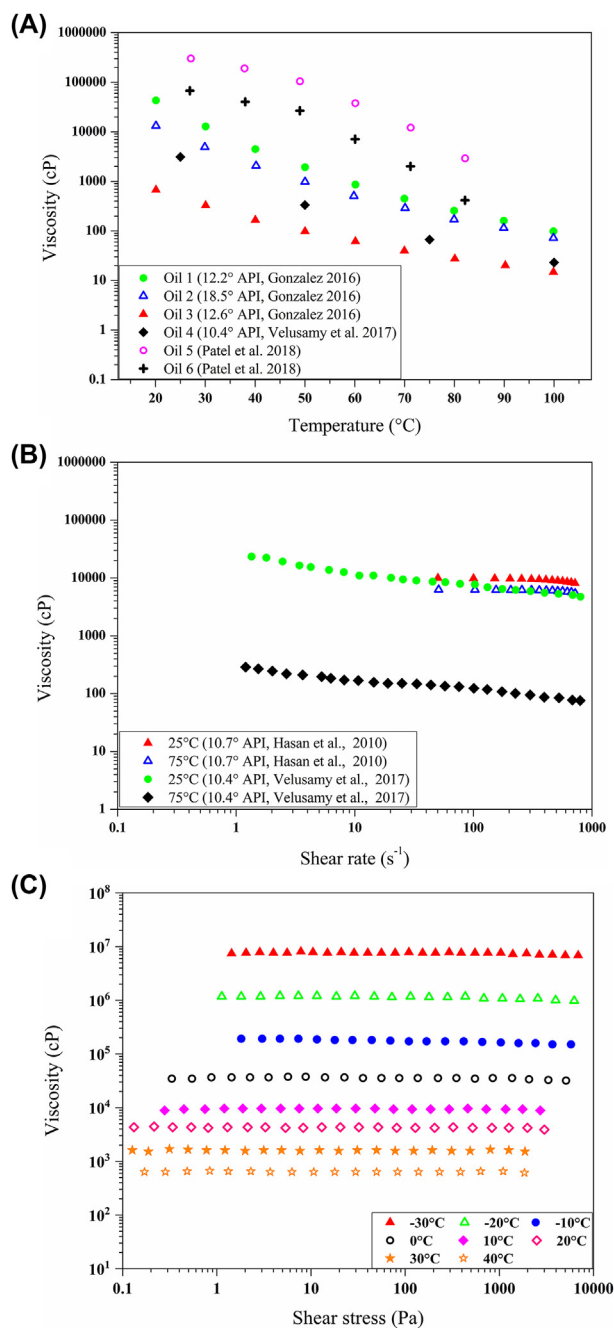


FIGURE 8.2

(A) Temperature effect on the viscosity of heavy crude oils. (B) Viscosity versus shear rate of heavy crude oils. (C) Dependence of viscosity on the shear stress for a heavy crude oil (15.1°API and asphaltene content of 7.5 wt%).

(A) Data adapted with permission from Elsevier (Patel et al., 2018) and American Chemical Society (Ramírez-Gonzalez, 2016; Velusamy et al., 2017). Copyright (Elsevier, 2018; American Chemical Society, 2016; 2017); (B) Data adapted with permission from Elsevier (Hasan et al., 2010) and American Chemical Society (Velusamy et al., 2017). Copyright (Elsevier, 2010; American Chemical Society, 2017); (C) Reproduced with permission from Elsevier (Ilyin et al., 2016), Copyright (Elsevier, 2016).

characteristics that affect the rheological properties of the crude oil are chemical and phase composition, the degree of dispersion of asphaltenes in the crude oil, the intermolecular and interparticle interactions between various particles present in the crude oil, etc (Bazyleva et al., 2010). The unusual properties of heavy crude oil, e.g., high viscosity or complex non-Newtonian rheological behavior, are primarily due to the asphaltene association (Lin et al., 1998; Luo and Gu, 2007).

3. Asphaltene and its impact on the rheology of crude oil

3.1 Introduction to asphaltenes

Asphaltenes are high molecular weight and polar fractions of the crude oil. As far as solubility is concerned, asphaltenes are insoluble in alkanes (that is lighter fractions such as n-pentane, n-heptane, etc.). In contrast, aromatic solvents like toluene are able to dissolve them (Akbarzadeh et al., 2007). A recent study on the solubility of heavy crude oil reveals that ionic liquids are able to dissolve the heavy crude oil in alkanes even in small quantities (Sakthivel et al., 2014). It is difficult to obtain asphaltene samples having the same or consistent properties because of the numerous reasons. Firstly, they represent a continuum of polynuclear aromatic species with increasing molecular mass and polarity (Alboudwarej et al., 2002). In addition, source and composition of the crude oils, polydispersity and the aggregation tendency of asphaltenes, and methods and solvents used to separate asphaltene have a major effect on the properties of the asphaltene separated (Acevedo et al., 2005). Furthermore, the discrepancies in the molecular weight determination of the asphaltenes could be due to association tendency of the asphaltenes even in dilute solutions (Moschopedis et al., 1976). For example, molecular weights ranging from 1000 to 300,000 Da (or g/mol) have been reported in past literature by using various techniques (such as monomolecular, ebullioscopic, ultracentrifuge, and vapor pressure osmometry method). From the laser desorption technique, the value was found to be not more than 2000 Da (or g/mol) with average value of around 400 Da (or g/mol) (Boduszynski, 1987; Miller et al., 1998). Table 8.2 lists the mass fractions of asphaltenes present in selected samples of crude oil and vacuum residue.

3.1.1 Separation methods

The separation of asphaltenes is dependent on several factors which are either chemical or physical in nature. These are listed as follows:

- a. Solvent (for precipitation as asphaltenes are insoluble in lighter and nonpolar fractions of crude oil, known as alkanes or paraffin).
- b. Temperature (speeds up the separation of asphaltene from the crude oil by increasing the motion of molecules resulting in more collisions).
- c. Aromaticity (comes from the polynuclear aromatic species present in heavier fractions and used for solubilization of asphaltene during separation process).

Table 8.2 Asphaltenes content of various samples including heavy crude oil, oil sand, and vacuum residue (S.G. stands for specific gravity).

Sample	Source	S.G.	API gravity	Saturates (wt%)	Aromatics (wt%)	Resin (wt%)	Asphaltene (wt%)
Assam heavy crude oil	Velusamy et al. (2017)	—	10.4°	26.4	64.8	4.1	4.7
South China sea crude oil	Sun et al. (2017)	—	11.4°	20.7	33.1	39.3	3.9
Athabasca bitumen	Hasan and Shaw (2010)	—	—	16.1	48.5	16.8	18.6
Maya crude oil		—	—	31.6	42.5	10.2	15.7
Buzurgan crude oil	Durand et al. (2010)	—	—	9.7	37.7	35.7	16.9
Maya crude oil		—	—	12.3	38.5	36.2	13.0
Athabasca crude oil		—	—	4.3	27.2	51.7	16.9
Cold lake vacuum residue	Hong and Watkinson (2004)	1.04	—	11.0	38.88	32.79	17.73
Athabasca tower bottom		1.02	—	20.68	44.3	19.3	13.1

- d. The molecular weight (higher molecular weight polar fractions of crude oil are insoluble in lighter, nonpolar fractions).

Some of the standards according to which asphaltenes are separated from sample using a required amount of solvent are mentioned below (Speight et al., 1984):

- a. ASTM D2007-75: 10 mL n-Pentane per gm of sample and 30 min of contact time.
- b. ASTM D2006-70: 50 mL n-Pentane per gm of sample and 15 h of contact time.
- c. Syncrude analytical method: 1 mL benzene per gm of sample followed by 40 mL n-pentane per gm of sample and 2 h of contact time.
- d. ASTM D893-69: 10 mL n-Pentane per gm of sample with 3 h of contact time.
- e. IP143/77: 10 mL n-Heptane per gm of sample followed by 1.5 h of contact time.

3.1.2 Composition and structure

Although the composition of asphaltenes extracted from various sources has similarity, the exact range is found to vary. For this reason, asphaltenes extracted from various samples show no consistency in properties. Table 8.3 shows the typical composition of asphaltenes separated from selected sources (heavy crude oils, oil sands, and vacuum residues). The amount of carbon and hydrogen varies over a narrow range. However, the H/C ratio remains almost constant. This leads to belief that

Table 8.3 Elemental composition (in wt%) of asphaltene samples extracted from various sources^a.

Sample	Year	C	H	N	S	O	H/C
Buton oil sand	Zheng et al. (2017)	75.06	7.86	0.83	8.35	7.91	1.26
Liaohe vacuum residue		86.32	8.3	2.19	0.29	2.91	1.16
Vene vacuum residue		82.85	7.93	1.82	5.06	2.35	1.15
Buzurgan crude oil	Durand et al. (2010)	81.2	7.2	1.1	8	0.9	1.07
Maya crude oil		83.5	7.2	1.0	5.8	0.9	1.04
Athabasca crude oil		80.6	7.7	1.3	8.4	1.4	1.15
Ratawi–Burgan vacuum residue	AlHumaidan et al. (2017)	81.61	7.62	2.04	8.73	—	1.12
Lower-Fars vacuum residue		80.10	7.33	1.94	1.84		1.098
Eocene vacuum residue		81.7	7.32	1.84	9.15	—	1.075

^a C, Carbon; H, Hydrogen; N, Nitrogen; O, Oxygen; S, Sulfur; H/C, Atomic ratio.

the unchanged asphaltenes have a fixed composition (Speight, 2004). As asphaltenes are a fraction of crude oil, some of the factors that play an important role in the composition of asphaltene are as follows (Barker, 1985):

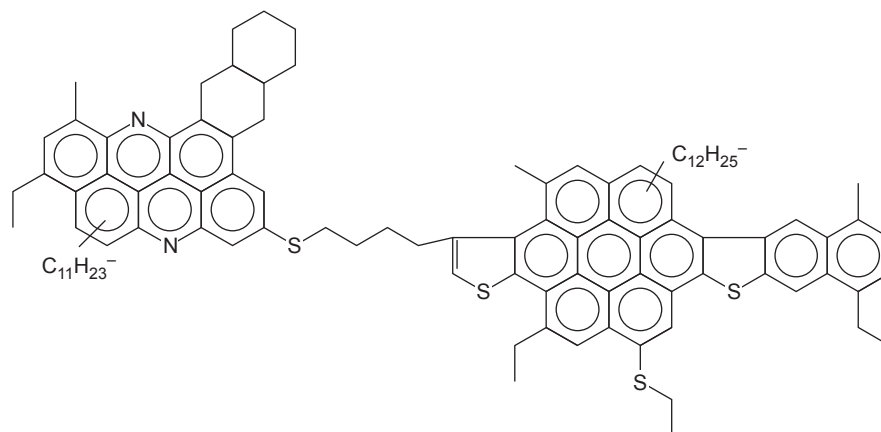
- a. The organic matter initially available in the source rocks.
- b. The conditions prevailing at the time of hydrocarbon generation. This plays a very important role.

As opposed to carbon and hydrogen contents of asphaltene, the heteroatom content varies noticeably. The amount of oxygen in asphaltene generally varies from 0.3 to 4.9 wt% and sulfur content varies from 0.3 to 10.3 wt%. The nitrogen content, on the other hand, varies to a lesser degree (0.6–3.3 wt%). Exposing asphaltene samples to atmospheric oxygen can substantially alter their oxygen content due to oxidation (Speight and Moschopedis, 1982). Similarly, contact of crude oil with sulfur minerals can lead to sulfur uptake thereby increasing its percentage in asphaltenes.

The structure of asphaltene molecules can be found out by combining the results of various analytical techniques such as a spectroscopic method involving Fourier transform infrared, nuclear magnetic resonance, mass spectroscopy methods, and elemental analysis. The way in which the structural entities (i.e., polynuclear aromatic cores) are arranged inside the molecule of the asphaltene remains a subject of debate. This along with polydispersity and self-association nature of asphaltene aggregates causes problems in ascertaining the structure of the asphaltene. Another factor contributing to the difficulty in structure determination of asphaltenes is the fact that they are a solubility class; therefore, they may be an accumulation of a number of smaller structures with varying molecular weights. The detailed information regarding the difficulties in ascertaining the structure to asphaltene can be found in the literature (Speight, 2004, 2006). A proposed structure of the asphaltene molecule extracted from vacuum residue of Ratawi-Burgan crude oil from Kuwait is shown in Fig. 8.3 (AlHumaidan et al., 2017). The vacuum residue has API gravity of 3.2° and the asphaltene content of 14.6 wt%.

3.1.3 Polydispersity

Asphaltenes are a polydisperse fraction of the crude oil. This means that they can be split into subfractions based on the solvents used for the precipitation. For example, the use of nC_5 , nC_7 , and nC_{10} gives rise to subfractions, namely nC_{5-7} , nC_{7-10} , and nC_{10+} . n -Pentane insoluble asphaltenes include nC_{5-7} , nC_{7-10} , and nC_{10+} subfractions, whereas nC_{7-10} and nC_{10+} subfractions together are termed as n -heptane asphaltenes. n -Decane asphaltenes constitute only nC_{10+} subfractions (Tavakkoli et al., 2014). The solubility and phase behavior of asphaltene in the crude oil depends on the pressure, temperature, and composition of the crude oil. Polydispersity of asphaltene was examined by various experimental techniques like small angle neutron scattering (Ravey et al., 1988; Overfield et al., 1989) and gel permeation chromatography (Drushel and Schulz, 1980). Studies have indicated that asphaltene forms colloidal particles of different shapes, e.g., elongated, disc like, etc. (Sheu et al., 1992). Changes in the pressure, temperature, and composition of the

**FIGURE 8.3**

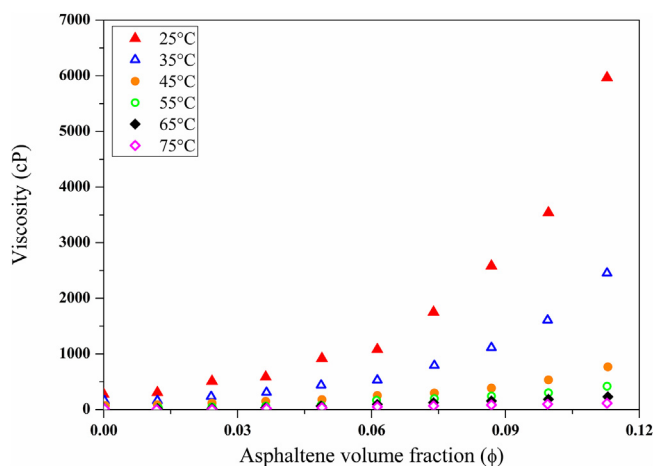
A proposed structure of the asphaltene molecule obtained from Ratawi-Burgan vacuum residue.

Reprinted with permission from American Chemical Society AlHumaidan, F.S., Hauser, A., Rana, M.S., Lababidi, H.M., 2017. NMR characterization of asphaltene derived from residual oils and their thermal decomposition. Energy Fuels 31 (4), 3812–3820. Copyright (American Chemical Society, 2017).

crude oil can destabilize this polydisperse fraction of the crude oil and cause aggregation and precipitation. Experimental techniques like optical microscopy have shown that these aggregates can grow from nanometer to micrometer length (Maqbool et al., 2009, 2011a, b).

3.2 Asphaltenes and its impact on the crude oil rheology

Asphaltene changes the microscopic flow behavior of the crude oil. Studies show that the presence of asphaltene results in higher viscosity of the crude oil. It was found that the viscosity increases exponentially with increase in asphaltene content of the crude oil (Fig. 8.4). In addition, the increase in viscosity with asphaltene content is more prominent at low temperature. Observation of glass transition has proven that asphaltenes are viscoelastic materials as observed by Zhang et al. (2004) and Ilyin et al. (2016). In addition, the presence of asphaltene in crude oil causes it to show viscoelastic behavior. The elasticity seems to be caused by the association tendency of asphaltene which creates an elastic network within the crude oil (Abivin et al., 2012; Ilyin et al., 2016). The viscoelasticity can also be found in waxy or paraffinic crude oil due to microstructures formed by the aggregation of paraffin wax crystals (Visintin et al., 2005). However, the viscoelasticity of crude oil caused by the presence of asphaltene is quite different than the viscoelasticity of waxy crude oil. The rheological response can be characterized with the dependency of storage modulus (G') and loss modulus (G'') on the angular frequency of deformation. Fig. 8.5 shows storage and loss moduli as a function of frequency of

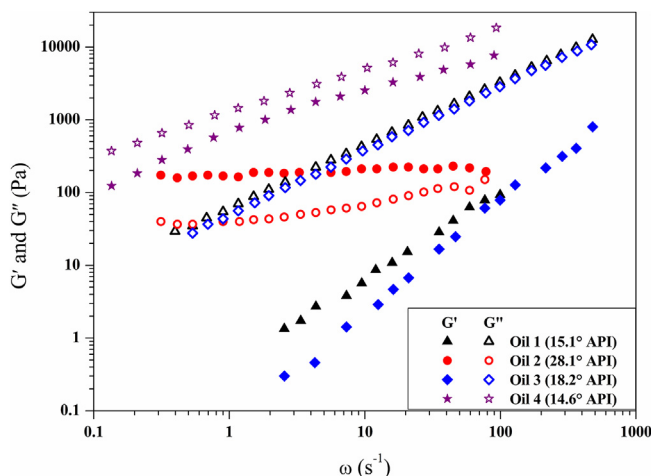
**FIGURE 8.4**

Viscosity versus asphaltene volume fraction of asphaltene in model heavy oil sample at six different temperatures.

Reproduced with permission from American Chemical Society Ghanavati, M., Shojaei, M.J., Ramazani, S.A.A., 2013 Effects of asphaltene content and temperature on viscosity of Iranian heavy crude oil: experimental and modelling study. Energy Fuels 27 (2), 7217–7232. Copyright (American Chemical Society, 2013).

deformation for four different crude oils, respectively. Crude oils with API gravity values ranging from 14 to 28° were obtained from various oilfields of Russia (Ilyin and Strelets, 2018). Storage and loss moduli were observed to be dependent on the frequency of deformation as shown in Fig. 8.5. In addition, the loss modulus (G'') exceeds the storage modulus (G'). However, for some crude oil (for example, oil 2 in Fig. 8.5), the storage modulus is independent of the frequency of deformation due to higher wax content which forms an aggregate structure and responsible for solid-like behavior. For such oil, the storage modulus exceeds the loss modulus.

The frequency dependency of the storage and loss moduli of heavy crude oil is also affected by the temperature. Unlike waxy crude oil which loses the viscoelasticity at higher temperature due melting of paraffin waxes, heavy crude still possesses viscoelasticity at higher temperature. However, the storage and loss moduli decrease with increase in temperature. Fig. 8.6A shows the effect of temperature on the frequency dependency of storage and loss moduli. The heavy crude oil has 4.7 wt% asphaltene content and 10.4° API gravity. It can be seen that the storage modulus decreases with an increase in temperature from 25 to 100°C. This can be due to the fact that at high temperatures the wax content dissolves, thus the crude oil loses its elasticity. On the other hand, loss modulus remains the same from 50 to 100°C as shown in Fig. 8.6A. At higher temperature, the loss modulus tends to remain constant when the frequency of deformation is low. As viscoelasticity is reflective of internal structure of the material, this type of behavior of heavy crude oil indicates some internal structures formed by heavier fractions of the crude oil.

**FIGURE 8.5**

Dependence on the frequency of storage modulus G' and loss modulus G'' of deformation at 0°C for five different crude oils.

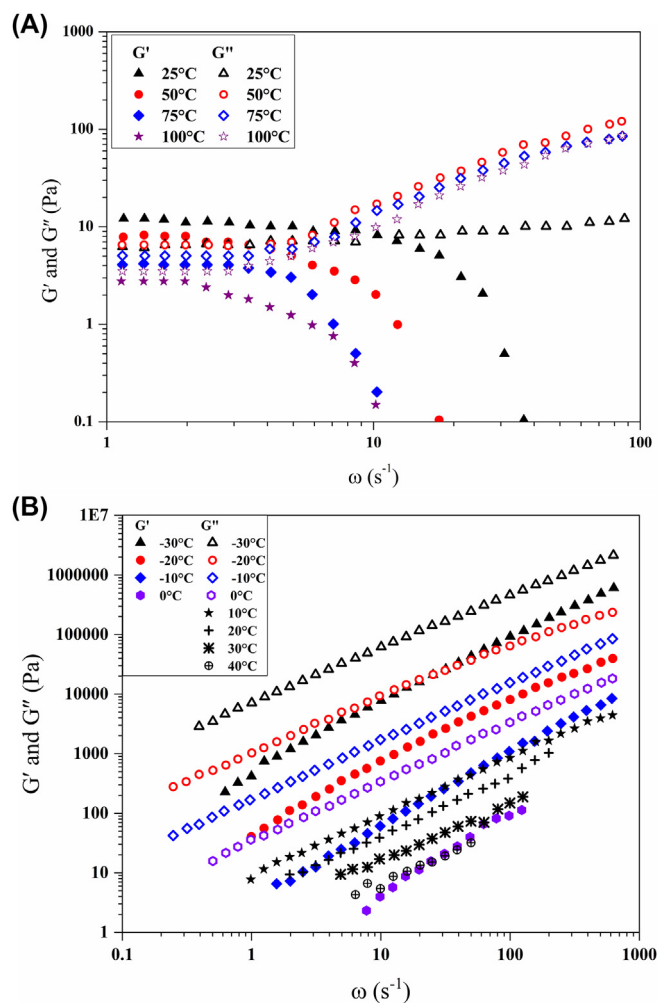
Reproduced from with permission from American Chemical Society Ilyin, S.O., Strelets, L.A., 2018. Basic fundamentals of petroleum rheology and their application for the investigation of crude oils of different natures. Energy Fuels 32 (1), 268–278. Copyright (American Chemical Society, 2018).

However, as discussed in Section 2.1, there have been cases where the heavy crude oil possesses Newtonian behavior over wide range of temperature and yet has viscoelastic behavior. The rheological characterization tests revealed that crude oil has zero elasticity above 0°C . The frequency dependency of the G' and G'' for this heavy crude oil sample is shown in Fig. 8.6B. It is clear from Fig. 8.6B that G'' remains almost increasingly linear throughout frequency range suggesting that the dynamic viscosity is constant. In addition, the Cox–Merz rule (for homogenous polymer melts) is well followed by the heavy crude oils due to the presence of asphaltene which have relaxation properties as discussed before.

4. Rheology of polymer-asphaltene composites and applications

4.1 Introduction to polymer composites

Polymer composites are made up of a polymer and a filler (which is added to improve their desirable properties). The resulting blend formed by the melt mixing technique has micro- and macrostructural improvements thereby enabling it to possess unique physicochemical properties. Mechanical properties such as strength and stiffness depend greatly on the rheology of the filled polymers. Therefore, the

**FIGURE 8.6**

Storage modulus and loss modulus versus frequency of deformation of a (A) heavy crude oil (4.7% asphaltene and 10.4° API) at 25°C, 50°C, 75°C, and 100°C. (B) heavy crude oil (7.5% asphaltene and 15° API).

(A) Reproduced with permission from American Chemical Society Velusamy, S., Sakthivel, S., Sangwai, J.S., 2017. Effects of imidazolium-based ionic liquids on the rheological behavior of heavy crude oil under high-pressure and high-temperature conditions. *Energy Fuels* 31 (8), 8764–8775. Copyright (American Chemical Society, 2017); (B) Reproduced with permission from Elsevier Ilyin, S.O., Arinina, M.P., Polyakova, M.Y., Kulichikhin, V.G., Malkin, A.Y., 2016. Rheological comparison of light and heavy crude oils. *Fuel* 186, 157–167. Copyright (Elsevier, 2016).

knowledge on the rheology of polymer composites becomes very important for analysis and optimization of their properties.

Polymer composites can be categorized on basis of the nature of matrix, filler, and the particle size. Fillers are additives, suspended in the continuous polymer phase (also known as matrix). Particles in the size 1–100 μm fall in the category of non-Brownian particles and give rise to microcomposites, whereas the particles in the size range of less than 100 nm belong to Brownian particles and give rise to nanocomposites (Rueda et al., 2017). Peclet number (P_e) is dimensionless number that describes the transition between the Brownian and non-Brownian particles in a suspension and is indicated by Eq. (8.2):

$$P_e = \frac{\dot{\gamma}}{D_{ro}} \quad (8.2)$$

Here, $\dot{\gamma}$ is the shear rate and D_{ro} is the rotary diffusivity of the particle (Larson, 1999). It gives rise to two types of behavior. At high P_e , shearing forces overcome the Brownian motion and particles come in close contact with each other, where the suspension becomes thick due to increase in the hydrodynamic forces caused by clustering of the particles. At low P_e , shear thinning happens because of the decrease in the strength of the structural arrangement of particles as compared with flow strength. This happens because of the decrease in the Brownian forces (Foss and Brady, 2000). High solid content with particle sizes greater than several 100s of nm is needed to obtain highly filled composites. The problem with nanocomposites is that although they exhibit stronger filler to matrices bond, they cannot achieve higher levels of filling due to fractal formation because of very high interfacial area (Rueda et al., 2017).

Highly filled polymers are used in many industries such as electronics packaging, batteries, ceramics, etc. (Azoug et al., 2014). As discussed before, the properties of the polymer composites are dependent on the properties of constituents. Addition of particles increases some mechanical properties like elastic modulus of composites up to a particular point because the particles themselves are more rigid than the polymers. After this point, the strength of the composite starts to decrease because the concentration of particles is too high to form a bond with polymers (Mohandesi et al., 2011). Properties of composites are dependent on the properties of the fillers such as size and shape, nature of interactions and linking with the fillers, and its orientation (Fu et al., 2008).

4.1.1 Filler properties

(a) Particle geometry: Particle geometry plays an important role in defining the processing and properties of the resulting polymer composites. The fillers are categorized into three groups, viz., needles (tubes), sheets (blocks), and spheres (Liang, 2013). The spherical shape of the filler is the basis for the development of mathematical model for describing the rheology of suspensions (Pan et al., 2009). However, the particles are rarely perfectly spherical in the actual case; therefore, a term known as aspect ratio (A_r) is used to define the deviation from the ideal shape.

It can also be described as the ratio of largest characteristic length to a minimum (Cassagnau, 2013).

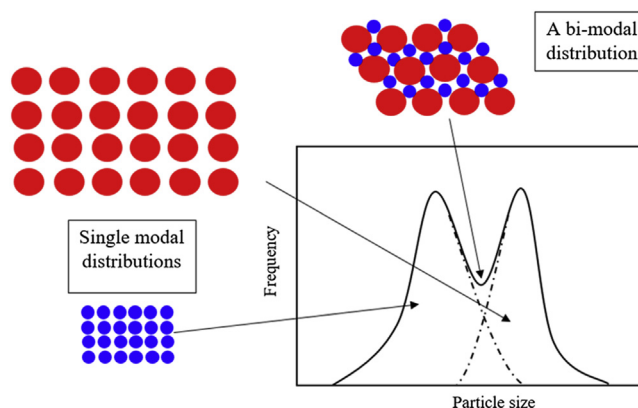
(b) Packing fraction and percolation threshold: It is of interest to keep loading as high as possible keeping the viscosity in control in industrial applications, where there is an emphasis on energy and cost savings. The maximum packing fraction (ϕ_m) is defined as the ratio of bulk density to the true density of the filler particles (Mayadunne et al., 1996). As the definition suggests, it is dependent on the filler geometry. A simple formula describing the relative viscosity (η_r) as a function of volume concentration of solids was first proposed by Roscoe (1952). Mooney et al. (1951) gave one of the most commonly used equations to predict the zero-shear viscosity of a particle suspension as:

$$\eta_r = \frac{k\phi}{1 - \frac{\phi}{\phi_m}} \quad (8.3)$$

Where k is the empirical parameter. The relative viscosity is the ratio of suspension viscosity to that of suspension medium at same shear stress. According to Eq. (8.3), the solid loading is limited by the maximum packing fraction. The relative viscosity will approach infinity as the volume fraction (ϕ) approaches ϕ_m . Various authors have used the value of ϕ_m by assuming different packing schemes. The list is given below:

- $\phi_m = 0.74$, assuming rhombohedral packing (Honek et al., 2005).
- $\phi_m = 0.52$, assuming simple cubic packing (Ting and Luebbbers, 1957).
- $\phi_m = 0.64$, assuming random closed packing of spheres (Nielsen, 1977).
- $\phi_m = 0.68$, spherical packing (Kitano et al., 1981), although the maximum value ranges from 0.625 to 0.641 (for close random packing for spheres), even smaller for aggregates and nonspherical particles as ϕ_m decreases with increase in aspect ratio of the particles.

The relative viscosity can be related to the particle concentration and the PSD (particle size distribution). It is easy to infer that η_r will increase with the increasing particle concentration and reach infinity at ϕ_m , asymptotically. This value ϕ_m can be found out from the graph between $(\phi\eta_r/(\eta_r-1))$ versus (ϕ) (Chong et al., 1971). Mathematical models such as Milewski's packing concept (Milewski and Katz, 1987) and simulations for finding the optimum composition of filler (Lee et al., 2006) or the hard packing by Torquato and Stillinger (2001) have been developed in attempts to determine the ϕ_m . For conductive fillers, there is a particular point known as percolation threshold (ϕ_c) after which the filler particles will begin contacting with each other. This increases the viscosity of the polymer composite. The maximum packing fraction (ϕ_m) can be increased further if we use a bimodal or a multimodal system because with the variation in the particle size, as there are high chances of particles being placed in the interstices between two large particles thus increasing the packing density. A schematic of how a single or bimodal system looks like is given in Fig. 8.7. It can be seen that there are 2 distinct peaks

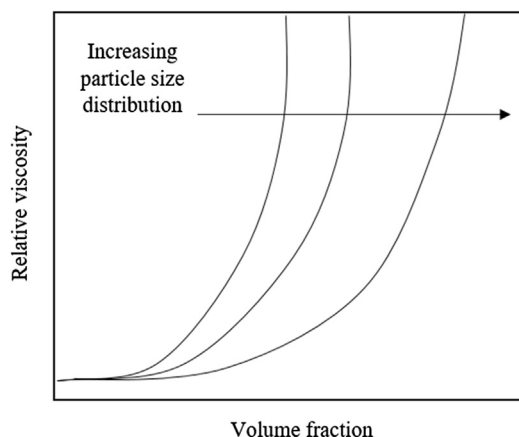
**FIGURE 8.7**

Schematic of the unimodal and bimodal distributions.

Adapted and modified with permission from Elsevier Hong, J.P., Yoon, S.W., Hwang, T., Oh, J.S., Hong, S.C., Lee, Y., Nam, J.D., 2012. High thermal conductivity epoxy composites with bimodal distribution of aluminum nitride and boron nitride fillers. Thermochim. Acta 537 (10), 70–75. Copyright (Elsevier, 2012).

corresponding to 2 different particle sizes that is single modal systems. The bimodal system on the other hand has small sized particles to fit easily in the interstices between the larger ones, thus increasing the packing density.

(c) PSD (Particle size distribution): The viscosity of polymer composite is strongly dependent on the PSD of the fillers (Metzner, 1985). For example, in a bimodal system, the fillers can reduce the viscosity. They also increase the packing density as described previously. It has been found that dilute systems with a packing fraction (ϕ) of less than 0.2 are affected by the PSD. There is a dearth of experimental studies on the filler-polymer melt suspension. Firstly, it is difficult to simulate a wide range of filler particle sizes because of their attrition during the mixing process. In addition, as opposed to the high concentration of the filler, the relative viscosity of low filler concentration polymer composites seems to be independent of the blend ratio. But viscosity improvements can be done with increased solid level by controlling the blend ratio of the polymer and filler particles. For highly filled systems, at 50% vol ratio, the viscosity was observed to be minimum for 80% of the coarse particles. In addition, the PSD has little effect on the viscosity for filler loading of 20%. Fig. 8.8 shows the effect of volume fraction of filler particles on the relative viscosity of a polymer composite. It can be seen that for a fixed volume fraction of the filler particles, the viscosity of the polymer blend decreases with an increase in the PSD of the filler particles. This happens because there is a wider range of filler particle sizes available, therefore more space for the particles to move around thereby lowering the viscosity of the polymer composite. With a constant particle size, an increase in the concentration of the filler particles will affect the relative viscosity of the composite due to interparticle interactions.

**FIGURE 8.8**

A schematic diagram showing the effect of volume fraction of the filler particles on the relative viscosity of the polymer composite.

(d) Interaction forces: Interpretation of the flow properties, particularly during polymer processing, is affected by interaction forces within the composites. It is generally difficult to define the interactions, especially in highly filled polymer system because of several forces which have to be accounted for. These can be categorized into Brownian, colloidal, and viscous forces. According to [Metzner \(1985\)](#), in the presence of highly viscous fluid (more than 10^3 P), the interparticle forces will be negligible, as a result the particles will truly act as suspended particles. When the particles are close enough, the colloidal forces are significant, therefore there will be a particular concentration above which the interparticle forces become significant. The interparticle force becomes significant only when the viscosity of the suspension is very less (of the order of few poises). Brownian forces are significant in dilute and semi-to-dilute regime and for very small concentration of particles in low viscosity solution. The viscous forces are significant for large particles ($>1\ \mu\text{m}$). Usually, the viscous forces dominate over colloidal forces for molten filled polymers until the value of ϕ is sufficiently high ([Bigg, 1983](#)).

4.2 Asphaltenes as fillers

Asphaltenes are regarded as the undesirable or waste product of the petroleum industry. They are one of the culprits for flow assurance where pipeline blockage problem can cause millions of dollars in damage. As described in Section 3, the properties of asphaltene extracted from various sources are inconsistent from sample to sample of crude oil. An estimate of molecular size using fluorescence depolarization techniques yielded the range to be around $10\text{--}20\ \text{\AA}$ ([Groenzin and Mullins, 1999](#)). Thus, they fall into the category of Brownian filler particles. The use of asphaltene as a filler for polymer composites has only recently been started to explore.

The thermoplastic polymers have established themselves in a huge number of applications like automotive, clothing and packaging industry, home furnishing, etc. The following section will take a look at some of the asphaltene-polymer composites and their properties. To get a clear picture and understanding of the different aspects of these composites, the study has been categorized into preparation, the rheological analyses, and finally results and discussions.

4.2.1 Preparation

A look into recent works on various asphaltene composites reveals melt mixing as the method of choice for the preparation of polymer composites. This method does not need any solvent and requires the polymers to be heated to glass transition temperature (T_g), and thereafter, the filler addition follows. The filler that is asphaltene aggregates are broken down and uniformly dispersed in the polymer matrix by the shear stresses generated by application of viscous drag. Table 8.4 shows some of

Table 8.4 Different polymer-asphaltene composites prepared by melt mixing method.

Source	Polymer	Filler loading		Composite use
Siddiqui et al. (2018)	LDPE (low-density polyethylene)	wt%	2.5	Containers, tubes plastic bags, and moulded equipment, etc.
			5	
			7.5	
			10	
			15	
Siddiqui (2017)	PP (polypropylene)	wt%	2.5	Containers for eatables, medicine, bottle caps and closures, etc.
			5	
			7.5	
			10	
			15	
Wu et al. (2016)	SBS (styrene-butadiene-styrene) triblock copolymer	wt%	5	Asphalt road construction
			10	
			20	
			30	
			40	
Siddiqui (2016)	MMA (methyl methacrylate)	mg per 5 mL of polymer	50	Lightweight shatter-resistant alternative to glass.
			2	
			5	
			7.5	
			9	
Siddiqui (2015)	PS (polystyrene)	mg per 5 mL of polymer	10	Applications involving thermal properties
			2	
			5	
			7.5	
			9	
			10	

the asphaltene-polymer composites prepared by melt mixing technique with different amounts of loading.

4.2.2 Rheological properties

As the mixing of filler and polymer is carried out, there is a change in the rheological behavior. This is achieved because of the formation of the filler network via reorganization of the particles within the composite. DMA or dynamic mechanical analysis technique is used to measure these properties. Important viscoelastic properties are as follows:

- i. Storage modulus (G') which gives information about the load transfer property. It represents the elastic portion.
- ii. Loss modulus (G'') which gives information about the viscous properties of the composites.
- iii. $\tan\delta$ which gives a measure of the viscous to the elastic portion of the composite.

The glass transition temperature is one of the most important properties of any polymer or polymer composites. It is the temperature at which the polymers/polymer composites undergo a transition from glassy, hard material to a soft rubbery or viscous state. The thermal transition can be defined in terms of free volume changes or relaxation time. A basic approach assumes the molecule to be composed of small moveable segments. As the temperature increases, the ability to move in various direction increases resulting in lower modulus or greater compliance. It is characterized by α and β transitions.

Fig. 8.9 shows the variation in the storage modulus with an increase in temperature. As the composite first warms, the side chain movement of the polymer occurs. This is known as the gamma transitions (T_γ). As the temperature is further increased, the whole side chain, as well as localized atoms, begins to move, giving

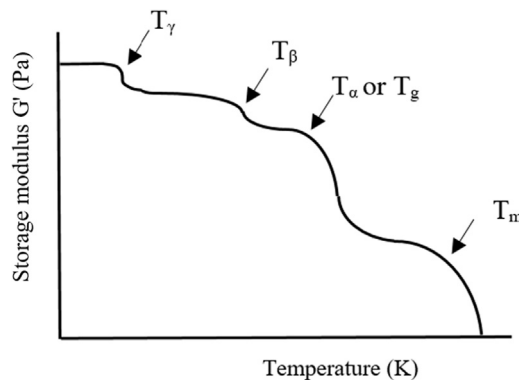


FIGURE 8.9

Schematic of the variation in the storage modulus of a polymer with temperature.

some stiffness to the composite. This is called beta transition (T_β). This T_g , although not clearly defined, is the T_g of the secondary component in the polymer blend. Further increase in temperature leads the polymer to ultimately reach T_m , where the large-scale chain slippage happens and polymer blend melts. There are sub T_g transitions also, but these can be too weak sometimes to be detected by the DMA and dielectric analysis (DEA) techniques. Although a correlation exists for T_β , it is not always an indicator of toughness (Boyer, 1968). This phase can be considered to be the deformation or activation barrier for sweep flow. Table 8.5 lists the glass transition temperatures PS (polystyrene) and MMA (methyl methacrylate) asphaltene composites corresponding to various methods. It is clear from Table 8.5 that the glass transition temperature stays around 66°C for polystyrene-asphaltene composites. For MMA-asphaltene composite, it ranges from 100°C to 108.6°C. There is an increase in the T_g values of the composites with an increase in loading of asphaltene. This is evident in case of MMA-asphaltene composite though not entirely clear for PS-asphaltene composite. The glass transition temperature (T_g) data for PS-asphaltene composites at different values of mass changes (i.e., at 10% and 50% weight change and residue) showed increasing trend in T_g with increasing filler concentration suggesting an improved filler matrix interaction. In addition, the glass transition temperature was maximum for composite with filler concentration at 3 wt-vol% suggesting

Table 8.5 Glass transition temperatures for PS-asphaltene and MMA-asphaltene composites corresponding to various methods (Siddiqui, 2015, 2016).

	Sample/system	PS-asphaltene			MMA-asphaltene
		Thermal method (DSC)	Loss modulus	$\tan\delta$	$\tan\delta$
T_g (°C)	Neat	66	74	87	100.0
	Composite1 (2 mg/5 mL) ^a	67	87	97	106.6
	Composite2 (5 mg/5 mL)	69	81	94	108.6
	Composite3 (7.5 mg/5 mL)	68	86	96	102.7
	Composite4 (9 mg/5 mL)	68	77	95	105.4
	Composite5 (10 mg/5 mL)	67	77	96	100.0

^a For e.g., 2mg/5 mL represents 2 mg of asphaltene sample per 5 mL of the polymer.

that it to be optimum filler concentration for PS-asphaltene composite. The G'' (loss modulus) data for temperatures ranging from 30 to 130°C show a shift in the peak to right due to improved interactions between matrix and filler. For the MMA-asphaltene composite, maximum T_g (glass transition temperature) was observed for filler concentration of 5mg/5 mL in MMA-asphaltene composites suggesting that this is the optimum concentration. This was also due to the strengthening of filler matrix interactions. Siddiqui et al. (2018) conducted a characterization of LDPE-asphaltene composites for determination of the reinforcement of the polymer blend. They observed the increase in the tensile strength and storage modulus to be significant for the sample with 5 wt% asphaltene, while the higher concentrations deteriorated these properties. These values have been summarized in Table 8.6.

Table 8.6 Mechanical properties and DMA properties of the LDPE-asphaltene composites with different wt% of asphaltene (Siddiqui et al., 2018).

System	Tensile strength (MPa)	Breakpoint elongation (times original length)	Storage modulus @ 23°C (GPa)	β relaxation (K)
LDPE (low-density polyethylene)	9.25	1.49	0.96	269.65
LDPE-asphaltene composite (2.5 wt%)	9.56	1.53	1.17	267.15
LDPE-asphaltene composite (5 wt%)	9.76	1.68	1.06	269.15
LDPE-asphaltene composite (7.5 wt%)	9.20	1.34	0.71	270.15
LDPE-asphaltene composite (10 wt%)	9.42	1.35	0.61	270.15
LDPE-asphaltene composite (15 wt%)	9.05	1.37	0.57	273.15

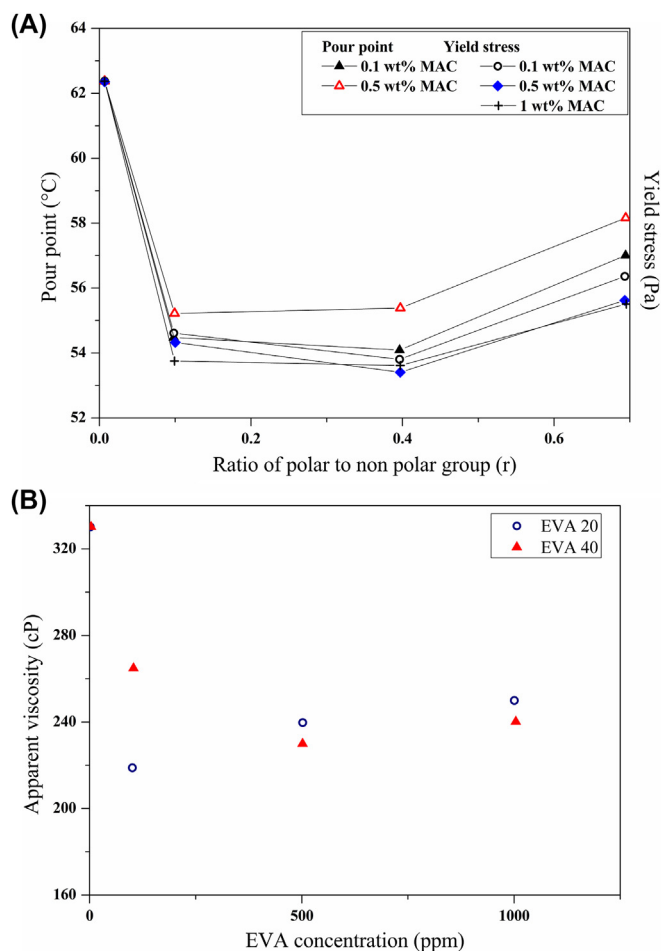
5. Polymer blends as a flow improver of heavy/waxy crude oil

As discussed in the previous section, crude oil is a complex mixture of hydrocarbons containing paraffins, aromatics, resins, and asphaltenes. The offshore reservoir pressure and temperatures are high enough (70–150°C and 8000–15,000 psi) to keep the asphaltene fractions dissolved in the crude oil. As the crude is being transported through pipelines, temperature changes (that is, it drops to much lower temperature) and leads to wax and heavier hydrocarbon separation and deposition (Singh et al., 2001). This phenomenon can be aggravated near the seabed condition where the temperatures can be around 4°C. This deposition of heavier hydrocarbons, primarily, waxes, and asphaltene can aggravate the flow assurance issues for oil and gas industry. Polymers can play a major role in combating the problem related to flow assurance issues. Several studies in the past have been done to assess the impact of polymers on the flowability of crude oil. These studies are summarized in Table 8.7. The effect of the polymers on the flowability of crude oil is mainly realized by their ability to change the crystallization of the paraffins and/or prevent the aggregation of asphaltenes. The polymers on addition to crude oils reduce the size of wax crystals and are also responsible for the reduction in the yield stress and pour point of the crude oil-polymer blend (shown in Fig. 8.10A) due to their assembly behavior. The crude oil (density of 867.6 kg/m³, 38.5 wt% wax, and 15.6 wt% asphaltene) was obtained from Liaohe oilfield, China. Here, (r) indicates the ratio of polar to nonpolar groups in the MAC (maleic acid alkylamides-co- α -octadecene) molecules. From Fig. 8.10A, it is clear that 0.5 wt% MAC polymer with r ratio of 0.4 has the highest depression in the pour point. For the same concentration, MAC polymer with r ratio of 0.4 shows a depression of yield stress. The MAC polymer molecules co-crystallize with paraffin crystals and the polar groups in the polymer chains and can limit the size of the wax crystals. MAC polymers also accumulate on the surface of asphaltene aggregates and form a steric layer (through interaction between carboxyl, amide groups in MAC with the asphaltene), thereby improving the flowability of crude oil (Li et al., 2012).

From Fig. 8.10B, we can see that there is a significant decrease in the viscosity of crude oil with increase in EVA (ethylene-vinyl acetate) copolymers concentration but after a certain point, there is not much effect of polymer concentration. The waxy crude oil (28.5° API, 9.7 wt% wax and 2.8 wt% asphaltene) was obtained from oilfields of Iran and EVA20 and EVA40 (with VA, i.e., vinyl acetate content of 20 wt% and 40 wt%, respectively) copolymers were used. Further tests on pour point and rheological properties of crude oils with EVAs (with varying VA content and various molecular weights) revealed that the efficiency of the EVA copolymers was dependent on the molecular weight of the copolymers and the asphaltene content. High molecular weight EVA copolymers were found to be more effective in suppressing the pour point of crude oil with the low asphaltene content. The efficiency of the EVA polymers was also found to be dependent on the side chain length of the alkyl

Table 8.7 Studies involving various polymers used to assess the flowability of crude oils.

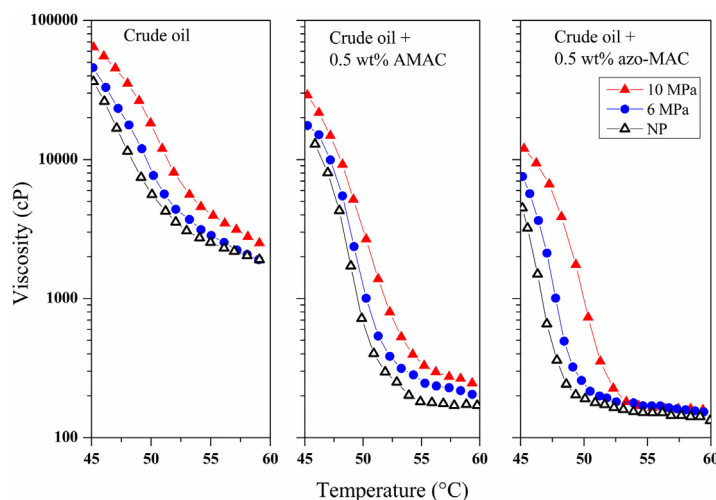
#	Crude oil type		Polymer used	Results	Source
1	Waxy crude oil		Poly (α -octadecene-co-maleic acid azobenzene amide) Azo-MAC	Yield stress reduction from 83% at 0.1 MPa to 95% at 10 MPa	Li et al. (2018)
	Wax (wt%)	39			
	Asphaltenes (wt%)	16			
	Viscosity @70°C (cP)	7.2			
2	Waxy crude oils		Methacrylate polymers	Decreased viscosity below pour point at high shear rates, high MW polymer more effective for low asphaltene content, and vice versa	Behbahani et al. (2017)
	Wax (wt%)	13–15.7			
	Asphaltenes (wt%)	0.13–0.3			
	Kinematic viscosity @40°C (cSt)	4.2–10.65			
3	Model waxy oils		Comb-type poly (maleic alkylamide-co- α -octadecene) copolymers	Improved flowability of the waxy crude oil due to assembly behavior and steric effect of the long chain alkyl branches	Xu et al. (2013)
4	Model waxy crude				
5	Waxy crude oils		Comb-type (maleic acid alkylamides-co- α -octadecene) copolymers	Reduced yield stress, improved flowability, maleic acid alkylamides-co- α -octadecene (MAC) acts as a polar amphiphile	Li et al. (2012)
	Wax (wt%)	5.2–13.21			
	Asphaltenes (wt%)	0.3–7.8			
	Kinematic viscosity @40°C (cSt)	7.8–15.1			
6	Light and heavy crude oils		Ethylene-vinyl acetate copolymer (EVA)	Viscosity reduction with high shear rate, lower mol. wt. EVA more effective for high asphaltene content and vice versa	Taraneh et al. (2008)
	Wax (wt%)	3.02, 3.83			
	Asphaltenes (wt%)	8.44, 15.7			
	Kinematic viscosity @25°C (cSt)	15.46, 198.56			
7	Waxy crude oils		Styrene (S), n-butyl acrylate (BuA), and vinyl acetate (VA) derived copolymers	EVA-excellent pour point depressant (PPD), reduced viscosity at high temperature, viscosity reduction influenced by the composition	Castro and Vazquez (2008)
	Wax (wt%)	10.3–11			
	Asphaltenes (wt%)	0.17–0.5			
	Dynamic viscosity (20–40°C) (cP)	~80–10			
			Alkyl fumarate-vinyl acetate copolymer	Can be used for high waxy crude oils containing 0.5 wt% asphaltene, efficiency limited by the molecular weight of the polymer	Borthakur et al. (1996)

**FIGURE 8.10**

(A) Pour point and yield stress of crude oil as a function r (ratio of polar to nonpolar molecule of the of MACs). The points at $r = 0$ mean without MACs added into model oil. (B) Viscosity dependence with polymer concentration at 5°C.

(A) Reproduced with permission from Elsevier Xu, J., Xing, S., Qian, H., Chen, S., Wei, X., Zhang, R., Li, L., Guo, X., 2013. Effect of polar/nonpolar groups in comb-type copolymers on cold flowability and paraffin crystallization of waxy oils. *Fuel* 103, 600–605. Copyright (Elsevier, 2013); (B) Reproduced with permission from Elsevier Taraneh, J.B., Rahmatollah, G., Hassan, A., Alireza, D., 2008. Effect of wax inhibitors on pour point and rheological properties of Iranian waxy crude oil. *Fuel Process. Technol.* 89 (10), 973–977. Copyright (Elsevier, 2008).

groups attached to the asphaltene molecules present in the crude oil. Different polar solvents like benzene, xylene, toluene, and CCl_4 were used to study the dilution and the effect of solvents on the viscosity of the crude oil. It was concluded from the results that using only solvents or flow improvers will result in the viscosity reduction less than solvent and subsequent addition of polymer (Taraneh et al., 2008).

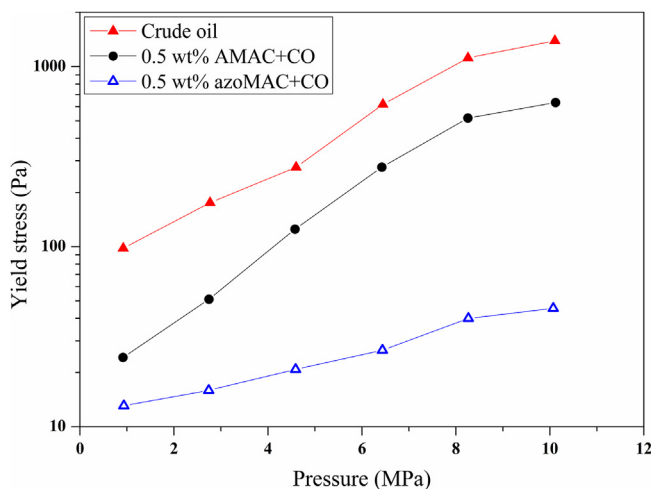
**FIGURE 8.11**

Viscosity–temperature relationship of crude oil before and after adding AMAC (α -olefin-co-maleic anhydride aniline) and azo-MAC (α -octadecene-co-maleic acid azobenzene amide) copolymers under normal pressures, 6 and 10 MPa.

Data adapted with permission from American Chemical Society Li, T., Wang, T., Xu, J., Zou, R., Si, Z., Becker, J., Li, L., Stuart, M.A.C., Prud'homme, R.K., Guo, X., 2018. Pressure Effect on the rheological behavior of waxy crude oil with comb-type copolymers bearing azobenzene pendant. *Ind. Eng. Chem. Res.* 57 (14), 4887–4894. Copyright (American Chemical Society, 2018).

Fig. 8.11 shows the effect of polymers on the viscosity–temperature relationship of the crude oil (density of 867.6 kg/m^3 , 39 wt% wax, and 16 wt% asphaltene) obtained from Liaohe oilfield, China. It is clear from Fig. 8.11 that the viscosity of the crude oil decreased with the addition of polymers (0.5 wt% AMAC and 0.5 wt% azo-MAC). The higher pressure has a significant increase in the viscosity for each of the polymer studied. However, in the case of the azo-MAC polymer, there is a significant decrease in the viscosity as compared with AMAC and no polymer case. This proves that the azo-MAC polymer performs better than the AMAC polymer in viscosity control of the heavy crude oil, especially at higher pressure (10 MPa).

Fig. 8.12 shows the growth in yield stress of crude oil with and without the addition of the MAC and azo-MAC. The increase in pressure increased the yield stresses monotonically. The increase in yield stress is much less for 0.5 wt% azo-MAC in crude oil as compared with 0.5 wt% MAC proving its performance under high pressures. In addition, the wax appearance temperature (WAT) was studied under two different wavelengths of UV light (i.e., 365 and 500 nm). The value of WAT was found out to be the lowest in case of azo-MAC (between 48.75 and 49°C) when compared with AMAC (between 49.75 and 50°C) and crude oil (between 50 and 50.25°C) showing that azo-MAC polymer had the highest WAT suppression.

**FIGURE 8.12**

Yield stress of crude oils before and after adding Azo-MAC and AMAC under various pressures at 50°C.

Reproduced with permission from Li, T., Wang, T., Xu, J., Zou, R., Si, Z., Becker, J., Li, L., Stuart, M.A.C., Prud'homme, R.K., Guo, X., 2018. Pressure Effect on the rheological behavior of waxy crude oil with comb-type copolymers bearing azobenzene pendant. *Ind. Eng. Chem. Res.* 57 (14), 4887–4894. Copyright (American Chemical Society, 2018).

In addition, the high-pressure UV-vis analysis (up to 5 MPa and 280–600 nm wavelength) confirmed the change in the configuration of azo-MAC from trans to cis at higher pressure thereby disrupting the assembly of asphaltene and wax and hence alter the flowability of crude oil (Li et al., 2018).

The molecular weight of polymer also has some effect on its efficiency to increase the flowability of the waxy crude oil (Behbahani et al., 2017). The effect of methacrylate polymers was investigated on the rheology of waxy crude oil with different asphaltene content (33.05°API, 13 wt% wax, and 0.13 wt% asphaltene; 40.22°API, 15.7 wt% wax, and 0.3 wt% asphaltene). The rheological studies confirmed that for the temperatures (5, 10, 15, 20, and 40°C with flow improver (methacrylate polymer) concentrations of (500, 1000, and 2000 ppm), the viscosity of the crude oil decreased drastically with increase in the concentration of polymers in both the samples. Below the pour point, the reduction in the viscosity was found to be dependent on the concentration of the flow improver. However, it was found that lower molecular weight polymer showed more efficiency in depressing the pour point of the crude oil with higher asphaltene content indicating that asphaltenes behave as a natural flow improver of the crude oil. This was due to two reasons. Firstly, asphaltenes assemble on the wax crystals and limit their growth. In addition, crystal growth rate of higher molecular weight polymers is higher so it cannot co-crystallize with the reduced size wax crystal.

Fig. 8.13 shows the temperature effect on the viscosity of the light and heavy crude oil with addition of different polymers. The light crude oil (specific gravity of 0.8784 and asphaltene content of 8.44 wt%) and the heavy crude oil (specific gravity of 0.9262 and asphaltene content of 15.7 wt%) were obtained from the

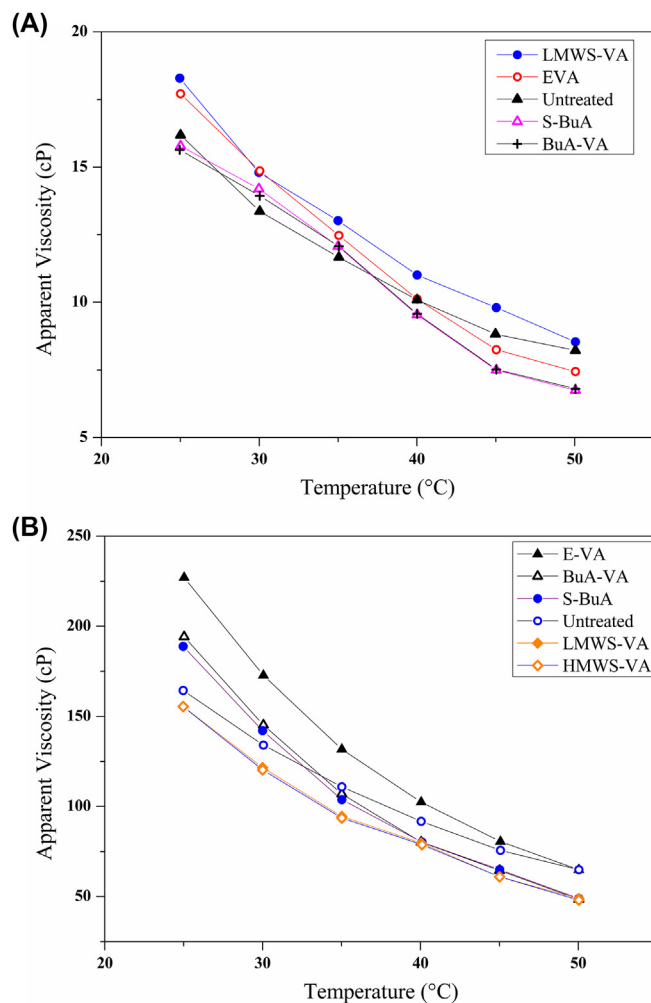


FIGURE 8.13

Temperature effect on the viscosity of (A) light crude oil (specific gravity of 0.8784 and asphaltene content of 8.44 wt%); (B) heavy crude oil (specific gravity of 0.9262 and asphaltene content of 15.7 wt%). E (Ethylene); VA (vinyl acetate); BuA (n-butyl acrylate); S (styrene); and LMWS/HMWS stand for low molecular weight and high molecular weight styrene, respectively.

Reproduced with permission from American Chemical Society Castro, L.V., Vazquez, F., 2008. Copolymers as flow improvers for Mexican crude oils. *Energy Fuels* 22 (6), 4006–4011. Copyright (American Chemical Society, 2008).

oilfields of Mexico. It is clear from Fig. 8.13 that the EVA copolymer improved the viscosity of light crude oil only in high temperature region. In addition, the use of flow improvers was only suggested for heavy crude oil and not light crude oils as the viscosity reduction is very limited as evident from the results.

6. Conclusion

This chapter dealt with the details on the asphaltenes and their impact on the heavy oil rheology. In addition, the use of asphaltenes as a filler for the polymer composites has been discussed. Asphaltenes are a waste product of the petroleum industry, but they can be useful for modifying the desirable properties of the polymers. They improve the viscoelastic properties. The storage modulus is improved due to their compatibility effect with polymers thereby enabling the better load transfer due to the strengthening of the filler matrix. However, the increase in storage modulus is found to be optimum up to a certain concentration after which it starts deteriorating. Polymers can also be used to improve flowability of heavy and waxy crude oils. This happens because of change in the nature of crystallization of the paraffin and reduction of yield stress. In addition, the asphaltene aggregation can be disrupted by conformational change of the polymer or it can be limited by steric hindrance due to interaction between various functional groups present in the polymers with the polar asphaltenes. They may also show good pour point depression. The chain length of the alkyl groups attached to asphaltene molecules plays an important role in the efficiency of the flow improver. It was also found in some cases that asphaltenes behave as a natural flow improver of the crude oil because they impeded the formation of large wax crystals.

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Rheology of hydrogels

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Abstract

Hydrogel is a general term used for water swollen and porous materials of polymeric, protein, peptidic, colloidal, surfactant, or lipid origin. Hydrogels are a mainstay in the food and pharmaceutical industries but are also increasingly finding applications in areas such as biosensing, microfluidics, drug delivery, and tissue engineering. Rheology is an appropriate method for characterizing hydrogel mechanical properties since it is quick, sensitive, requires small sample sizes, and is revealing of differences in architecture such as degree of cross-linking, proximity of the glass transition, structural homogeneity/heterogeneity and molecular weight. In this chapter we are discussing various aspects of rheology of hydrogels.

Keywords: Cross-link hydrogels; Hydrogel; Rheology; Rheometer; Small amplitude oscillatory shear; Smart hydrogels.

Hydrogel is a general term used for water swollen and porous materials of polymeric, protein, peptidic, colloidal, surfactant, or lipid origin. Hydrogels are a mainstay in the food and pharmaceutical industries but are also increasingly finding applications in areas such as biosensing, microfluidics, drug delivery, and tissue engineering (Peppas et al., 1986).

The name hydrogel consists of the words *hydro* and *gel* that translates to aqueous (water-containing) gels. Hydrogels are materials that have three-dimensional structure, which entrap a large amount of water. Hydrogels are polymeric and hydrophilic materials in which the amount of water is up to 90% (Barbucci, 2008). Hydrogels consist of polymer networks that are insoluble in water. The polymeric network is hydrophilic, and polymers are held together by covalent bonds. In structure there are weaker cohesive forces such as hydrogen and ionic bonds and intermolecular hydrophobic interactions (Kishida and Ikada, 2001). There are plenty of different hydrogels with different chemical structure of the constituting polymers. Hydrogels can be tailored to respond to external stimuli, such as temperature, pH, electric field, light, solvent composition, ionic strength, salt type, light, pressure, and specific biomolecules. Hydrogels which are environmental-sensitive are often called “smart hydrogels.” They respond (i.e., swell, shrink, bend, or degrade) to changes in environmental conditions. One main property of “smart hydrogels” is that they change their swelling ratio rather abruptly on small changes in environmental factors. Thermoplastic hydrogels are physical gels; they are based on linear copolymers

of hydrophilic and hydrophobic monomers. Thermoplastic hydrogels are easy to process due to their hydrophobic interactions between hydrophobic chains of the copolymer. They also dissolve in organic solvents but swell without dissolving in water. Hydrogel foams are developed to overcome slow swelling of hydrogels. Usually the equilibrium swelling takes from hours to days depending on the size and the shape of hydrogels. Hydrogel foams have a porous structure that is made by synthesizing hydrogels in the presence of gas bubbles. The size of the pores in the hydrogel foams is larger than in hydrogel sponges or microporous hydrogels. Hydrogel foams have much faster kinetics and extent of swelling than other hydrogels because water is absorbed into hydrogel foams by capillary reaction through the pores. Hydrogel foams are useful in many biomedical applications in which the property of fast swelling with a very large swelling ratio is required.

Hydrogels are not perfect biomaterials; therefore, they still cause foreign body reactions. In addition, hydrogels have rather poor mechanical strength and durability for some biomedical applications.

A broad classification of hydrogels based on the type of cross-linking is commonly made, i.e., chemically (covalently) cross-linked or physically cross-linked (based on secondary interactions such as hydrogen bonding, hydrophobic and electrostatic interactions). The highly hydrated and porous nature of hydrogels in general can be leveraged for their utility as encapsulating agents and delivery devices for therapeutic agents such as cells, growth factors, DNA, and drugs.

An important property of hydrogels relevant to their applications such as drug delivery vectors, tissue engineering scaffolds, or biomedical implants and biosealant was that it can be injected using a simple device such as a syringe or a catheter. A large number of studies have been focused on injection of liquid precursors that are injected at a desired site into the body and then undergo designed sol–gel transition (via physical or chemical mechanisms) at the site of delivery and thus solidify post injection. These materials have the capacity to encapsulate therapeutic agent and cell payloads as a consequence of gelation at the site of delivery. Although injectable delivery of liquid precursors is a widely studied strategy, they have some limitations. Liquid precursors injected at a desired site of delivery in the body are subject to dilution with bodily fluids or leakage into neighboring tissue. Owing to these factors, mechanical properties of the hydrogels formed from these precursors might be compromised, and toxicity concerns might arise because of the presence of unreacted initiators, cross-linking agents, and uncross-linked polymers. Injection of liquid precursors offers little control over flow properties, spatial location, and biological response of uncross-linked liquid precursors immediately after injection. This lack of control can lead to potential ambiguity in desired performance of *in vivo* hydrogels in terms of established *ex vivo* parameters such as specific morphology, drug/protein release profile, and encapsulated cell biological behavior.

The rheological characterization is a widely used and convenient strategy for investigating shear response of solid injectable hydrogels. Studying the shear response of solid injectable hydrogels in terms of exact flow profile and potential changes in hydrogel bulk structural characteristics is a step forward in understanding the shear behavior of solid injectable hydrogels (Hamidi et al., 2008). Physically

cross-linked hydrogels, which form the hydrogel class representing most solid injectable hydrogels, have been reported to demonstrate diverse behavior such as bulk fracture, strain stiffening, and shear banding when subjected to large amplitude oscillatory or steady-state shear. Rheological characterization provides information about the changes in mechanical behavior of physically cross-linked, solid, injectable hydrogels. It is often not possible to obtain correlations between mechanical and morphological behavior of physically cross-linked hydrogels when subject to shear solely by the use of rheometric experiments. In this chapter, we discuss the use of a confocal-rheometer compound assembly that provides a direct visual evidence of the flow pattern of a solid injectable peptide hydrogel sample under steady-state shear. The rheometer-induced shear treatment in the experiment reported herein is very similar to that reported in citations in the previous paragraph that discuss shear thinning and rehealing behavior of physical hydrogels.

1. Principles of rheology

1.1 Rheological behavior of materials

Rheology is literally “flow science.” The word “rheology” originates from the Greek word “rheos” which means “the river,” “flowing” and “streaming.” Rheological experiments do not only mean study the flow behavior of liquids but also the deformation behavior of solids. The connection between these two is that large deformations are caused by shear forces and those shear forces cause many materials to flow (Mezger, 2002). There are several fields where rheology plays an important role, such as quality control, production and application, chemical and mechanical engineering, materials science, and industrial research and development. The aim of rheology is to examine the rheological properties of several materials such as polymers, adhesives, paints, paper coatings, foodstuff, cosmetics, pharmaceuticals and medicaments, surface technology, ceramic, glass, and metal casting. Rheological properties have a huge effect on the processability and the final properties of a product. Depending on the final purpose of the product, it is important to study the flow and the deformation behavior of materials and how they react in target purpose and in target environment. All forms of shear behavior can be viewed as lying in between two extremes such as the flow of ideal viscous liquids and the deformation of ideal elastic solids. The behavior of real materials is a combination of both the viscous and the elastic behavior, it is called viscoelastic behavior. Wallpaper paste is an example of a viscoelastic liquid, and a gum eraser is an example of a viscoelastic solid.

For ideal elastic material, the deformation occurs immediately after the stress is applied (the strain is independent of time) and the deformation recovers completely after the external stress is released. Elastic deformation is instantaneous. For ideal viscous behavior, the deformation or strain is not instantaneous; in response to an applied stress, deformation is delayed or dependent on time. The deformation of viscous material is irreversible. In viscoelastic materials, part of the deformation occurs immediately after the external stress is applied and part of the deformation

is delayed (Dash et al., 2013). Hydrogels are also capable of sustained release for drug or gene therapies and can provide an injection vehicle/temporary scaffold for cell-based therapies (Hamidi et al., 2008). For all these applications (Ta et al., 2009), understanding and properly quantifying the underlying mechanical properties of hydrogels, such as equilibrium modulus and gelation time, is of critical importance.

Rheology is an appropriate method for characterizing hydrogel mechanical properties because it is quick, sensitive, requires small sample sizes, and is revealing differences in architecture such as degree of cross-linking, proximity of the glass transition, structural homogeneity/heterogeneity, and molecular weight. There are a number of reviews of the rheological properties of hydrogels composed of proteins (Ross-Murphy and Shatwell, 1993), polysaccharides, or both (Yan and Pochan, 2010).

The main rheological technique to characterize hydrogels is small amplitude oscillatory shear (SAOS). In SAOS, a small amount of sample (<1g) is placed between parallel disks or a cone and a disk, and a small amplitude torsional oscillation generates shear flow in the sample. In the linear viscoelastic (LVE) technique, the frequency dependence of the dynamic moduli may be used to deduce important aspects of gel structure and mechanical behavior. For example, with frequency sweeps, we can detect gel character, entanglement, and the glass transition, and some details of chain architecture (Morrison, 2001).

The viscoelastic properties of Si-HPMC (Silated hydroxypropylmethylcellulose) hydrogel examined as a function of time and polymer concentration shows the storage (G') and loss (G'') moduli and damping factor $\tan(\delta)$ (G''/G') values as follows. The storage modulus of hydrogel increases with increasing polymer concentration. The hydrogel showed storage moduli of 200 and 400 Pa at 1.5% and 2% (w/v), respectively. Under these conditions, the loss modulus only increases from 12 to 18 Pa when increasing concentration. Therefore, the damping factor $\tan(\delta)$ of hydrogel decreased with increasing polymer concentration, showing the formation of higher network densities at higher polymer concentration. Si-HPMC solution exhibits a viscous behavior and can be classified as a macromolecular solution. Percolation theory was applied to determine the gel point and to discuss the dependence of G' and G'' on frequency during sol–gel transition. The gelation depends on buffer volume used to neutralize the Si-HPMC solution. Gel point ranges from 300 to 1300 s, depending on the buffer solution ratio (2/1 and 1/1 (v/v), respectively). After 3 weeks of cross-linking, the Si-HPMC hydrogels were elastic with a storage modulus ranging from 200 to 400 Pa.

1.2 Rheological characterization of physical and chemical gelatin gels

The physical and chemical gels were swollen outside the rheometer, before application on the plate of the rheometer. Although apparently a good contact was obtained between the swollen gels and the plates of the rheometer at low compression, it was

likely that this was not so, due to the inhomogeneity of the surface of the hydrogels. The structure of the sandpaper had to be pushed into the hydrogel to establish perfect contact between the sandpaper and the hydrogel. On compression of the gelatin gels, the normal force kept increasing. As outlined in the methodological section, G' was measured after each compression step. G' increased until it leveled off, and only changes of a few percent were observed on further compression. The systematic compression of the gelatin gels resulted into very reproducible G' profiles (Axelos and Kolb, 1990; Bourges et al., 2002).

Rheological characterization of peptide and polypeptide-based hydrogels relative to aspects of bulk mechanical and viscoelastic properties, observations of gelation mechanisms, and the behavior of hydrogels during and after flow were studied by Conggi Yan and et al. Fundamental principles and applications of hydrogels in general have already been discussed thoroughly in a number of comprehensive reviews (Dash et al., 2013; Hamidi et al., 2008; Ta et al., 2009; Ross-Murphy and Shatwell, 1993; Yan and Pochan, 2010; Morrison, 2001; Kopecek, 2007; Lin et al., 2015), and so this material will not be repeated here. Mechanical properties are criteria growing in importance as to judge the feasibility of a hydrogel for a specific biological application (Hamidi et al., 2008; Seitz et al., 2009; Davaille et al., 2010). For example, the gel has to be rigid enough to sustain itself as a scaffold for cell growth while appropriate mechanical stiffness is essential for regulation of cell phenotype, cell adhesion, and cell gene expression (Waffle, 2016). Proper flow properties allow hydrogels to be excellent candidates for injectable therapeutic delivery vehicles if they shear-thin on the application of a proper shear stress and rapidly self-heal into solids once the stress is removed. In this case, solid, preformed gels are capable of being delivered to a targeted *in vivo* site by simple syringe injection (Kopecek, 2007). On removal of injection shear, immediate recovery of gel stiffness enables payloads (e.g., therapeutics) that were encapsulated during hydrogel formation to remain localized against *in vivo* biological forces (Davaille et al., 2010; Vallée et al. 2009). Finally, fundamental understanding of gelation mechanisms helps unveil the pathways of forming a network, inspiring further development of hydrogels for tissue repair and drug delivery (Sun et al., 2013).

The primary experimental method with which researchers explore the viscoelastic properties of hydrogels is rheology. Importantly, equipment to perform the basic rheological exploration of hydrogel materials is inexpensive and fits on the bench top of any biomaterial's laboratory. The field of rheology theory, measurements, and equipment is well introduced in books on the subject, e.g., by Macosko and Mezger. However, we would like to briefly describe the very basics of what hydrogel properties can be measured with rheology as these properties are frequently discussed in the remainder of the article.

To assess mechanical properties quantitatively, primarily small deformation rheology experiments are performed on biopolymeric hydrogels. By small deformation, the measurement is meant to be carried out within linear viscoelastic region of a material, ensuring the measured hydrogel properties are independent of the magnitude of imposed strain or stress. Typical small deformation tests are SAOS

measurement as well as creep and creep recovery tests. There are a few examples of the former gelation mechanism. The Ulijn group reported hydrogelation of Fmoc-functionalized amino acids initiated under physiological conditions. Fmoc-diphenylalanine (Fmoc-F₂) molecules were found to self-assemble into fibrous hydrogels that support 3D cell culture of living cells. Mechanical rigidity of Fmoc-F₂ gels were tunable via functionalization of the network with different chemical moieties. The resulting gel networks displayed optimized compatibility with various cells. Xu and coworkers also presented a series of Fmoc-dipeptides, of which the sol-gel transition was reversible in response to shift in temperature and pH. In addition, the same group reported hydrogelation in response to the binding of vancomycin where gel stiffness was observed to increase significantly. Mahler et al. demonstrated that diluting an Fmoc-F₂ stock solution in water to a proper concentration initiated sol-gel transition, leading to Fmoc-F₂ gels that were shear thinning. Recently, Adams et al. reported that gelation of Fmoc-dipeptides was induced by hydrolysis of glucono- δ -lactone. The resulting hydrogels were homogeneous, and their mechanical properties were reproducible regardless of the preshear history they experienced.

Carbopol has been used in laboratory experiments of shear zone evolution by Schrank et al. (2008) as analog of strain softening rocks to investigate the relationship between shear zone geometry and rheology. In this case, the authors selected Carbopol because the non-Newtonian flow behavior favors strain localization as shear zones in nature. Most of these shear zones show strain softening, and thus they will be easily reactivated. This softening is important for the stress distribution within the lithosphere. Non-neutralized samples at a concentration of 5.0 wt.% develop narrowing shear zones and show a progressive increase of localization intensity after yielding when shear is applied. The width of the shear zone decreases as a function of strain, while both the incremental and the cumulative localization of intensity factor increase as a function of strain. The experimental results confirmed previous observations where shear softening rocks were associated with shear zones that narrow progressively.

Balmforth and Rust explored how the steady and weakly nonlinear, overtiring solutions of the Newtonian Rayleigh-Bénard (RB) problem are modified when the fluid is non-Newtonian (Lin et al., 2015). The same authors performed laboratory experiments on a layer of Carbopol 940, with concentrations of 0.05 and 0.1 wt.% heated from below and found that the yield stress inhibits convection, but a sufficiently strong perturbation can initiate overturning. Convection only starts if the yield stress, τ_0 , is “sufficiently low,” i.e., thermal instabilities develop without imposing any external trigger if that corresponds to low concentrated samples. Contrarily, higher yield stresses (concentrations ranging between 0.05 and 0.1 wt.%) do not lead to spontaneous convection if fluid is left undisturbed. Thermal convection initiates only if the system is perturbed by the injection of air bubbles at the base of the tank, or by forced mixing with a stirrer. A qualitative picture of magma convection is described, in which the yield stress of crystal-rich magma

prevents or delays the instability, and convection may be limited to the hotter (less crystalline) portions of the magma chamber.

The addition of glycerol into Carbopol fluids results in increasing the coefficient of thermal expansion and in diminishing the yield stress compared with samples mixed only with water and similar concentration of Carbopol. Three different regimes are distinguished by two critical values of the yield parameter, Y_0 , which compare the thermally induced stress, τ_{th} , to the yield stress, τ_0 , of the solution where P is the thermal power out of the heater, whereby the system operates at constant power supply, and α is the thermal expansivity. Recently, Carbopol with concentrations varying between 0.05 and 0.115 wt.% has been used to model the onset of thermal convection under different boundary (free-slip vs. no slip) and geometrical conditions (Seitz et al., 2009). Both authors observed both reversible (due to a supercritical bifurcation) and irreversible (subcritical bifurcation) behaviors but discrepancies are revealed from the comparison between the two works because of the employed experimental protocol, the boundary conditions, and the differences between the measured yield stress values despite the use of comparable Carbopol polymer concentrations (Davaille et al., 2010). The three rheological parameters, τ_0 , $K\dot{\gamma}$, and n , of the HB constitutive model cannot be varied independently when preparing a Carbopol solution. Hence, a detailed parametric study showing that the plume dynamics are governed by the interplay between yield stress, buoyancy-induced stress, and viscous stresses was conducted. If the buoyancy of the bubble is not sufficient to break the yield stress of the fluid, then the bubble remains trapped in the fluid indefinitely. For a given τ_0 , the inverted “tear-drop” shape of the static bubbles appears to be nonunique.

The rheological properties were measured by a rheometer. The measuring program that was used was oscillatory test. The amplitude sweep was used to define the LVE range for hydrogels. From the LVE range, the storage modulus and the loss modulus were determined. The complex shear modulus was then calculated by using the storage and the loss modulus. Additionally, the frequency sweep from LVE range was measured. The stress–strain curves for hydrogels were determined by a compression test. The Young’s modulus was calculated from the slope stress–strain curve. As an observation, the oscillatory test proved to be a more accurate measuring method than the compression test. The anisotropy of the sample structure caused variation of results and higher standard deviations. The compression test results were not affected by the anisotropy of the samples. The rheological measuring method turned out to be suitable for measuring the stiffness of the softer hydrogels. For the stronger hydrogels, on the other hand, the results had a high standard deviation. The reason for the high standard deviation is the anisotropy of the sample structure. The rheological moduli for gellan gum hydrogels were lower and the standard deviation higher than for the hyaluronic acid hydrogels (Waffle, 2016). As a conclusion from both measuring methods, the stiffness of the hydrogels became higher when the cross-linker concentration increased. The rheological measurement method was found to be suitable for the softer hydrogels. However, for the hydrogels

with the higher cross-linker concentration and the fast gelation time, the rheological measuring method needs further studies.

1.3 The yield stress, τ_0 .

Yield stress appears as the result of jamming of the swollen microgel particles at higher concentration values. As jamming transition occurs, steric interactions and entanglements form, developing the yield stress and an elastic modulus larger than the viscous modulus. The particle-tracking microrheology shows particle tracers moving in both viscous and viscoelastic environments. As concentration approaches 1.0 wt.%, the system is more or less closely packed and tracers are trapped in a growing elastic environment. Confocal fluorescence microscopy of dyed Carbopol dispersions reveals that at intermediate volume fractions, where dispersions are viscoelastic, Carbopol consists of a percolated structure of gel particles with significant void space. At higher concentration, Carbopol can be described by a fully space-filling paste of swollen microgel particles that are kinetically arrested by the contacts between neighbors and are not able to move through the solvent. This could explain the slowdown of τ_0 increasing rate as c rises from 0.5 to 1.0 wt%.

The rheological characterization of a material generally comprises both studies in the flow and oscillatory modes. Experiments in the oscillatory regime were performed with various amphiphilic alginamide derivatives, and the results were compared with those corresponding to the nonmodified polymer. A classical behavior was observed, with G' and G'' with increasing the substitution ratio due to the formation of hydrophobic associations in the aqueous system. With polymers at low substitution ratios, viscous solutions were obtained, with the loss moduli higher than the storage moduli, both being frequency dependent. These solutions exhibit typical viscoelastic behavior. However, G' and G'' do not vary as x^2 and x , as usually observed for a Maxwell fluid. This phenomenon is generally attributed to the superimposition of both the disentanglement of the polymer chains and the disengagement of the apolar segments from hydrophobic associations (Vallée et al., 2009). With polymers at substitution ratios higher than 9%, hydrogels were obtained, characterized mainly by an elastic behavior, i.e., G' is higher than G'' and is frequency independent. For polymers with substitution ratio higher than about 10%, the flow curves display at intermediate shear stress an inflection point in the shear thinning region with two critical stress levels (Sun et al., 2013). A similar behavior has already been observed. These results may indicate that the network structure is a function of the applied stress, such as a shear-induced structuring through hydrophobic junctions. It can also be seen as the mark of important heterogeneities in the nature of hydrophobic junctions between alginate chains. This result is in contrast to the rheological behavior of alginate ester solutions which exhibit classical properties of amphiphilic polymers where the decrease in viscosity with shear rate obeys a power law (Tirtaatmadja et al., 1997; English et al., 1997).

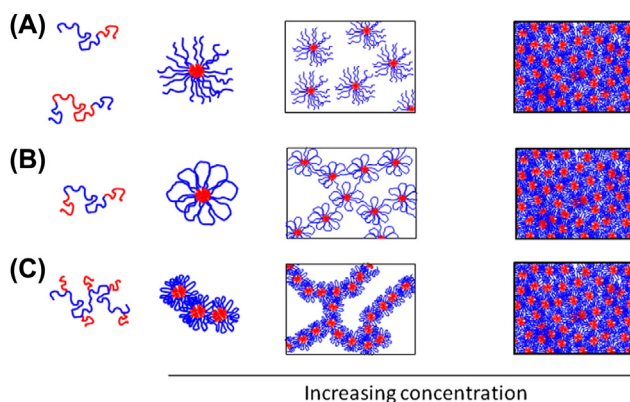
The rheological study of a series of PVAT dual cross-link hydrogels, permanently cross-linked by glutaraldehyde and transiently cross-linked by borate ions

(Shibayama et al., 1994), at various cross-linking densities, in comparison with the corresponding chemical gels were done and evolved the following conclusions (Sun et al., 2012).

- (1) **Additivity:** The contribution of the chemical and physical cross-links to the dynamic moduli was determined in torsion tests, and the additivity (independent and additive contributions of the two types of cross-links to the elastic and viscous moduli) was confirmed for all investigated systems. The dependence of the relaxation time on the physical cross-linking ratio was explained by the incomplete relaxation of the chain between two adjacent cross-links for low cross-link densities. When the healing timer association of open cross-links is shorter than the Rouse relaxation time of the chain, the rheological relaxation time slows down. Thus, the relaxation time can increase with decreasing physical cross-linking density due to the concomitant increase in the Rouse time and decrease in the healing time.
- (2) **Extensibility:** In all cases, the extensibility of the dual cross-link gels was found to be higher than that of the corresponding chemical gels. However, the benefit of adding physical cross-links decreased for higher physical cross-link densities, and the extensibility also decreased at fixed chemical cross-link density with increasing physical cross-linking density suggesting that the effect of the physical cross-links on the strain hardening may also play a role in the fracture (Guo et al., 2016).
- (3) **Separability:** The strong strain rate—dependent behavior of the stress measured in tensile tests could be simplified by separating its strain-dependent and time-dependent terms. The strain-dependent term was described by the neo-Hookean model, whereas the time-dependent term reflected the breaking and reforming dynamics of the physical bonds.

If the polymers contain more than one associating block, these blocks may assemble either into the same core forming loops or into different cores forming bridges between the multiplets. The simplest case is that of telechelic polymers that contain associating blocks situated at the ends of the chains. This situation is analogous to solutions of spherical colloids with a short range attraction and a more or less soft excluded volume interaction. Reversible aggregation leads to the formation of clusters that grow with increasing concentration until at a critical concentration they percolate into a space spanning transient network. Increasing the attraction at a fixed concentration leads to larger aggregates, but when the attraction is too strong, phase separation occurs into a low-density phase and a close packed densely cross-linked phase.

The rheology of transient networks is determined by the amount and the lifetime of the bridges. In the simplest case that the bridging chains are flexible and unentangled, each bridging chain contributes about 1 kT to the elastic modulus according to the theory of rubber elasticity. The introduction B—A—B systems can form transient networks of bridged multiplets. The rheology of these networks is determined by the concentration of the bridges and their lifetime. However, at higher

**FIGURE 9.1**

Schematic drawing of the aggregation of associating polymers with different topologies, the associating blocks (hydrophobic) are red and the solvophilic blocks (hydrophilic) are blue.

concentrations, repulsion between the multiplets can also play a role. The transient networks based on PMMA–PnBA–PMMA triblock copolymer in 2-ethylhexanol during compression were recently studied. The large strain behavior of the system was well described by a modified Gent model for unentangled polymer networks. A crack front instability was observed in gels of sufficiently long mid-blocks with cracks transforming spontaneously from rough to smooth with increasing speed. Finite element modeling showed that the stress field directly ahead of the crack tip was highly anisotropic and quite different from that predicted from linear elastic fracture mechanics (Seitz et al., 2009).

The rheological properties of associative polymers are important for many applications. In recent years, variety of the chemistry of both the solvophobic and solvophilic blocks has much increased to obtain associative polymers with particular properties such as biocompatibility or sensitivity to external parameters, e.g., temperature and pH. Mainly aqueous solutions have been studied in recent years, but associative polymers have also been used to thicken or gel ionic liquids (Prazeres et al., 2005). Polymers containing only a single associating group form most often small spherical multiplets. The rheology of these systems is determined by the repulsion between the solvophilic blocks that form the corona. At high volume fractions, jamming of aggregates leads to the formation of a gel. The strength of the gels and the concentration range where they are formed depend on the temperature and can be modified by adding polymers and, in some cases, by varying the ionic strength or the pH.

Complex hydrogels include nanostructured hydrogel, stimuli responsive hydrogels, hydrogels containing nanoparticles, micro- and nanogels, and composite hydrogel. Part of this activity is focused on the study of the rheological properties of complex natural hydrogels such as soft tissue of the human body to be able to mimic their properties. Complex and smart hydrogels are studied for different biomedical applications, as examples, in the ophthalmic field hydrogels are optimized

as tear substitutes, in cataract surgery as viscoelastic devices, in orthopedic field as viscoelastic agents for the restoration of the functions of the synovial fluid, in cosmetic surgery, fillers for the correction of skin imperfections, and fillers for injection into the paralyzed vocal fold are developed and studied in terms of rheological properties. Creep and stress relaxation tests are performed along with flow tests to obtain viscosity as a function of shear rate. Yield stress, yield strain, and properties such as thixotropy are also evaluated. All rheological properties are evaluated through the use of rotational and capillary rheometers. The rheological analysis is used, also, to study and optimize the gelation of polymeric systems which respond to external stimuli such as temperature and pH (polymer self-assembly) and to study the kinetics of gelation for systems photopolymerisable through UV and heat.

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Rheology of liquid crystalline polymers

10

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Abstract

Liquid crystallinity was invented in the 19th century. It was sometimes called the fourth state of matter because of the ability of macromolecules to generate liquid crystal phases. The main classification divided liquid crystalline polymers (LCPs) into lyotropic and thermotropic types. Interpretation of the rheological behavior of LCP is more complicated than for other polymers. Ordinary polymers are characterized by a normal stress effect in shear flow, which always has a positive sign. There is a visible impact of temperature, solvents, plasticizers, the macromolecular structure, and the average molecular weight on the rheological behavior of LCPs. This chapter approximates and describes the most characteristic rheological behaviors of LCPs.

Keywords: Lyotropic liquid crystalline polymers; Rheology of liquid crystalline polymers; Solution concentration impact; Temperature dependence; Thermotropic liquid crystalline polymers.

1. Introduction to liquid crystalline polymers

Liquid crystalline (LC) polymers (LCPs) consist of macromolecular chain and lower—molecular weight (LMW) molecules in the macromolecular structure that make orientational ordering possible whereas positional ordering is nonexistent. This orientational ordering can be formed by molecules characterized by shape anisotropy. They can be used to produce carbon fibers and plastic objects for electro-optical applications, data storage and detergents and cosmetics.

There are two main ways to classify LCPs. The first method is based on the position of LMW molecules that are responsible for orientational ordering. LMW molecules affect LC behavior and may be located in the macromolecular main chain or side chains. A generic scheme of main chain and side-chain LCPs is presented in Fig. 10.1. The mesogenic units can displayed as units shaped as a rod, board, disk, or bent core and may be part of the main chain or linked by spacers to the polymer backbone in a parallel or perpendicular position.

The second method is based on the mechanism for inducing transition from an isotropic to LC state and divides LCPs into lyotropic LCPs (LLCPs), and thermotropic LCPs (TLCPs). LLCP show mesomorphic behavior in a solution and feature six

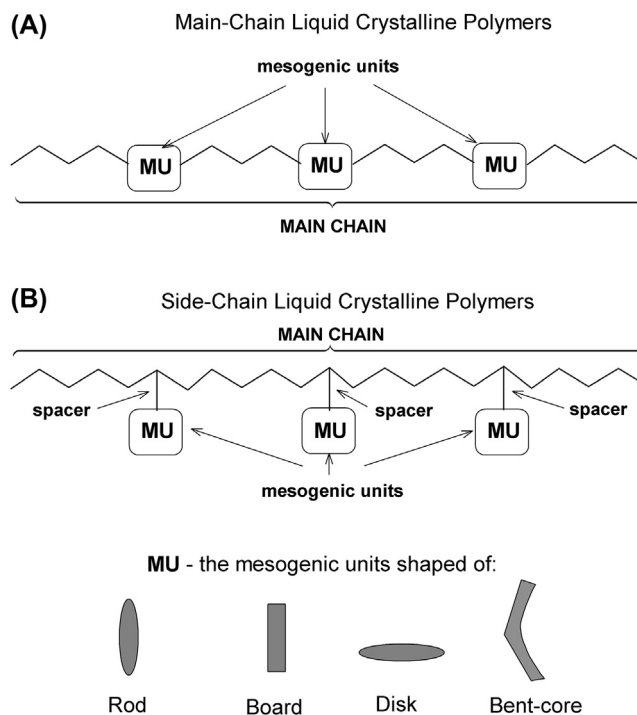


FIGURE 10.1

Scheme of main chain and side-chain liquid crystalline polymers. MU, mesogenic units.

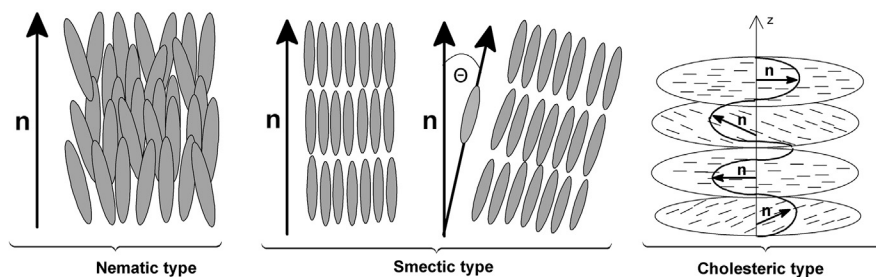


FIGURE 10.2

Three basic mesophases of liquid crystalline polymers: nematic, smectic, and cholesteric.

phases from low to high amphiphilic concentration. In the case of TLCP, in which mesomorphic behavior occurs at a defined temperature, LMW molecules responsible for liquid crystallinity can be divided into five phases: nematic, smectic, chiral, discotic, and bowlic (Mewis and Moldenaers, 1996a,b). Fig. 10.2 presents three main types of TLCP mesophases.

In the case of nematic LCPs with rod-like mesogenic units, order in the liquid crystal results from the orientation of elongated segments of the molecules. It is reasonable that dense packing of rigid rod-like molecules favors parallel alignment. Considering the nematic phase, the particles are characteristically organized randomly. Nematics (N) are often used for liquid-crystal displays because of high energy savings during their use; in themselves, they have a fibrous texture. N are characterized by the highest number of degrees of freedom, which results from the parallel segregation of all molecules along a single axis (Iwan, 2010; Urbanski et al., 2017). At the N phase, TLCPs can be easily processed. Viscosity decreases with an increase in temperature and low energy is required for processing N LCPs (Rahman, 2013). The properties of N result from their anisotropic behavior (depending on the observed direction), and typically, N can flow easily, but if the flow is along unit vector n (known as the director or optical axis) or perpendicular to it, or for the latter case, the flow velocity gradient is along vector n or perpendicular to it, that makes a difference (Urbanski et al., 2017). The director n as a vector determines only the direction of the preferred orientation of the molecules and indicates nothing about the degree of orientational order in the LC phase (Thakur and Kessler, 2015). To determine the degree of orientation, an order parameter S is experimentally assigned, defined in terms of the angle Θ of a molecular axis (Dealy et al., 1990) with respect to the director by the equation:

$$S = \frac{1}{2} (3 \cos^2 \Theta - 1) \quad (10.1)$$

Smectic LCPs are characterized by a complex molecular structure because, aside from orientational ordering, difference occur in positional order connected with molecule localization (Andrienko, 2018). Molecules in the smectic phases might be located in parallel or oblique in relation to the smectic ordering plane. In the case of type SmB, the beginning of ordering at the plane is observed. For this TLCP, mesophase classes are divided into the chiral and blue phase I, II, and III kinds. Blue phases occur at a narrow temperature range. Other classifications of smectic for TLCPs include the degree of molecules ordering as fluid state and crystal state (Shibaev and Plate, 1984; Iwan, 2010).

Although some kinds of LCPs are precisely described in the literature in terms of their morphological, thermal, and mechanical properties, there are far fewer articles focused on interpreting the rheological behavior of various types of LCPs, because such behavior of the LCPs is more complicated than for other polymers. Ordinary polymers are characterized by a normal stress effect in a shear flow, which has always a positive sign. For example, nematic LCPs have two sign reversals with an increase in the rate of shear (Marrucci, 1991). Furthermore, the impact of temperature, solvents, plasticizers, the macromolecular structure, and the average molecular weight is also seen on the rheological behavior of LCPs (Mewis and Moldenaers, 1987; Drappel et al., 1997). The aim of this chapter is to describe the most characteristic rheological behaviors of various type of LCPs.

2. Lyotropic liquid crystalline polymers and their rheological behavior

LLCPs are well-known and their properties depend on the ratio between the polymer and solvent and the polymer concentration. At the narrow range of the polymer content, at the point of critical concentration, phase changes take place. This process depends on the temperature; for this type of LCP, three main regions in the temperature–polymer concentration scheme can be considered. The theory indicates that lyotropic nematic liquid crystallinity is a consequence of chain stiffness and large overall shape anisotropy because of the rigid rods of molecules (Shibaev, 2016). At the range of critical concentration of the polymer, changes in viscosity are characteristic for LLCs. The viscosity increases with an increase in polymer concentration, and achieves a critical point, and then a slight decrease in viscosity of LLCs is observed.

Fig. 10.3 presents a theoretical tree-region phase diagram for rigid rod molecules. It is characteristic of lyotropic liquid crystals that at various temperatures, the concentration of crystal phases can change; on the other hand, at a constant temperature, different concentrations of rigid rods molecules can form an LC phase or not. The characteristic phase diagram divides LC phases into an isotropic phase, an anisotropic LC, phase and a mixture of the two phases. Region I in Fig. 10.3 shows an isotropic phase that forms for a low concentration of rods at various temperatures. After exceeding critical concentration under a higher temperature, the solution transforms into an anisotropic LC phase (Region II). Between these two phases, at a higher temperature, there exists a thin range of concentrations in which the solution creates a two-phase mixture called isotropic and anisotropic LC (Region III). This region is typical in the case of excess crystal concentrations at lower temperatures.

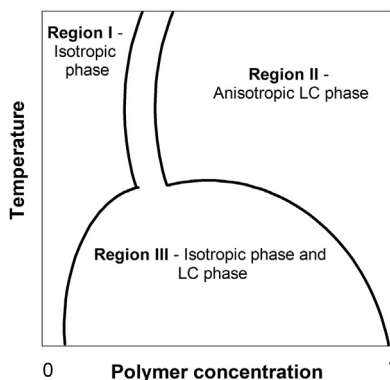


FIGURE 10.3

Scheme of theoretical tree regions of temperature–polymer concentration dependence for lyotropic thermotropic crystalline polymers. LC, liquid crystalline.

The scheme was adapted from Shibaev, V.P., 2016. *Liquid crystalline polymers*. In: *Reference Module in Materials Science and Materials Engineering*. Elsevier Ltd., pp. 1–46. <https://doi.org/10.1080/00914039108041090>.

The relation between the viscosity of the polymer solution and the polymer concentration (for both the stiff chain and soft chain polymers) can be described by modified Martin equation (Kulichikhin, 1989):

$$\eta_i = C(\eta) \exp K_M C(\eta) \left(\frac{C}{C_c} \right)^\beta \quad (10.2)$$

where η_i = relative viscosity increment; K_M = Martin constant; and C_c = concentration corresponding to the onset of interpenetration of the molecular coils.

One of the most well-developed materials that can form lyotropic liquid crystals in a solution is cellulose and its chemical derivatives. This is because cellulose macromolecules can form a chiral nematic structure with a left- or right-handed helicoidal arrangement. Various types of cellulose materials allow LCs to be obtained in different media and levels of concentration. Depending on the solution, three states of samples usually occur: isotropic, liquid crystals, and gel samples, which can be recognized and identified by rheological measurements. The resulting graphical relation of viscosity versus shear rate for a broad range of concentrations verified which solutions are related to the liquid crystal state. The characteristic viscosity profile for LC phases features three regions, as mentioned. Region I usually occurs at low shear rates and characterizes shear thinning. It is prompted by the alignment of liquid crystal domains along the shear direction. Region II appears at intermediate shear rates and is assigned to a plateau in which all LC domains are oriented along the shear direction. The last one, Region III, occurs at the highest shear rates, in which LC domains are destroyed by overscale shear stress and free crystals are layered along the shear direction, leading to shear thinning. Generally, the theoretical dependence of viscosity and shear stress can be easily explained based on the theory of Onogi and Asada. The scheme of the three-region logarithmic viscosity—shear rate curve of LCPs is presented in Subsection 3 in Fig. 10.9.

Determining the rheological behavior of LLCs encounters many problems. Many research articles have focused on this issue related to the high practical application of these materials. Shafiei-Sabet et al. (2014) studied the rheological behavior of cellulose nanocrystal (CNC) suspensions in deionized water and NaCl solutions at various concentrations. In previous work (Shafiei-Sabet et al., 2012; Shafiei-Sabet et al., 2013), the authors verified the impact of sonication and ultrasound energy (a method of CNC particle dispersion) and the effect of the degree of sulfation on the viscosity of CNC suspension. They confirmed that with an increase in ultrasound energy, the viscosity of these suspensions decreased. This is related to the formation of aggregates during sonication and their breakage with higher use of ultrasound energy. Moreover, the authors studied the relations between viscosity and CNC suspension concentration in deionized water. The results confirmed increasing viscosity with an increase in CNC concentration. Furthermore, the concentration of CNC suspensions influenced the profile of the correlation between viscosity and shear rate. Lower CNC concentration (up to 10 wt.%) caused that samples are characterized by a three-region profile whereas higher CNC concentration (above 10 wt.%)

materials revealed a single-region profile. The results enabled CNC suspensions to be divided into three kinds of samples: isotropic samples, liquid crystals, and gels. The authors confirmed the transition from isotropic samples to anisotropic chiral N liquid crystals for CNC suspensions from 3 to 10 wt.% concentration in deionized water solutions. The rheological behavior of CNC suspensions was also precisely described by other researchers (Jia et al., 2014; Li et al., 2015; Qiao et al., 2016; Oguzlu et al., 2017), confirming the three-region profile characteristics of LLCs.

The researchers also investigated ionic strength and the rheological behavior of CNC suspensions at various concentrations of NaCl solutions (Shafiei-Sabet et al., 2014). Based on the viscosity profiles, they divided different CNC suspensions at various NaCl solutions into three types: isotropic, anisotropic, and gel samples. The characteristic showed that this division agreed with the previous one. Isotropic characteristics in the viscosity profile for all NaCl concentrations characterized samples with a CNC concentration up to 3 wt.%. In this case, the rheological dependence of viscosity and shear rate revealed the same profile for all samples. The results also verified that with higher concentration of NaCl the viscosity decreased, which confirmed higher ionic strength. In the case of anisotropic and gel samples, the range from 4 to 10 wt.% and above 11 wt.% of CNC concentration, respectively, indicated the reverse dependence. Furthermore, the addition of NaCl to the CNC suspension from 7 to 10 wt.% decreased the amount of region from 3 for the CNC suspension in deionized water to a value of 2 for NaCl solutions from 1 to 5 mM. These changes are related to the lack of a plateau region in which all LC domains are oriented along the shear direction. Samples with higher concentration of NaCl are characterized by one-region viscosity profile thereby they indicate the state without LCs. The last case, gel samples, was characterized by shear thinning behavior over all shear rates and confirmed aggregation of CNC particles in solutions.

Denn et al. (Riise et al., 1999) investigated the rheological behavior of blends containing a flexible polymer matrix of was polydimethylsiloxane (PDMS) and various solutions of hydroxypropyl cellulose (HPC) used as a dispersed phase. They confirmed the impact of the HPC concentration in a water solution on the possibility of LC formation. They verified the occurrence of LC phases for a sample of 50% HPC solution in which the sample with PDMS and the sample with 35% HPC solution revealed isotropic characteristics during rheological measurements. In the next step, the authors investigated the rheological characteristics of blends with 10 wt.% of a 35 wt.% solution of HPC and 10 and 20 wt.% of a 50 wt.% solution of HPC. All prepared blends revealed shear thinning characteristics in which the highest viscosity indicated a sample with 20 wt.% of a 50 wt.% solution of HPC.

Peng et al. (2018) worked on the rheological behavior of rod-like CNCs solutions in water. They confirmed that the viscosity of CNCs solutions increased with an increase in the CNC concentrations, which indicated shear thinning behavior. Moreover, they verified that solutions with CNC concentrations higher than 4 wt.% revealed three-region characteristics of flow curves, which were described

previously. In the next step, the authors investigated the rheological behavior of CNC rod-like particles in a solution with polymeric systems. To four different concentration of CNC solutions, the added sodium carboxyl methyl cellulose (NaCMC), and hydroxypropyl methylcellulose (HPMC) at 1 and 0.02 wt.%, respectively. They claimed that the ideal elastic gel should be characterized by independent correlations between storage modulus G' and measurements of frequency and by a correlation between G' and loss modulus G'' equal to $G' > G''$. The results confirmed a weak dependence of G' and G'' and solid-like gel behavior for samples with 5 wt.% CNCs particles. Furthermore, the gelation behavior of anisotropic CNC dispersion in nonionic polymers such as polyethylene glycol, polyvinyl alcohol, and HPMC, anionic polymers such as NaCMC, sodium alginate, and gum arabic, and cationic polymers such as LMW chitosan, medium molecular weight chitosan MCHI, poly diallyl dimethyl ammonium chloride were investigated. The results indicated that the thickening effect had the trend: cationic > anionic > nonionic, which could be attributed to different interactions between CNCs and polymers as well as the molecular properties of the polymer chains.

Zheng et al. (2011) investigated lyotropic liquid crystals formed based on fish oil. With different ratios of system components, which were fish oil, food-grade emulsifier, and oil as a solvent, fish oil formed two types of lyotropic LC phases: hexagonal and lamellar. The authors confirmed that all fish oil liquid crystal systems had elastomer behavior. The differences were related to rheological characteristics, which for the lamellar phase was gel-like fluid and for the hexagonal phase was viscoelastic behavior. Furthermore, rheological measurements showed that storage modulus G' was bigger than loss modulus G'' in the linear viscoelastic region, which suggested that elasticity was more prominent than viscosity. Based on this investigation and according to work by other researchers, the authors verified the primary principles of the rheological properties of lamellar and hexagonal LCs:

- For lamellar LCs, which characterized gel-like structure system, the correlation between G' and G'' is constant and equals $G' > G''$.
- For lamellar LCs, the viscosity of a system decreases linearly with an increase in measurement of frequency.
- For hexagonal LCs, values of G' and G'' grow linearly with an increase in measurement of frequency.

Pal et al. (Singh et al., 2015) investigated novel lyotropic liquid crystals for control delivery applications based on a mixture of sorbitan monooleate, polysorbate, an aqueous solution of polyvinyl alcohol (10% w/w), and sesame oil. The gels were water in oil emulsions characterized by transparency. Four LLCs gels were prepared using two concentrations of sorbitan monooleate and polysorbate mixture and different polyvinyl alcohol solutions. Two samples from this were used as a matrix for metronidazole. Rheological measurements indicated that both materials with different concentrations of sorbitan monooleate and polysorbate mixture had thixotropic behavior with shear thinning. Moreover, it was verified that a higher amount of sorbitan monooleate and polysorbate mixture in the gel led to a higher viscosity

value. Nevertheless, the authors claimed that prepared gels had good stability and biocompatibility and metronidazole could be released by diffusion, verifying the possibility of applying LLC gels in drug delivery system.

[Shimamoto and Gray \(1998\)](#) investigated the formation of mesophases by ethyl cellulose and (acetyl ethyl) cellulose in solid films. These compounds are part of LLCs characterized by LMW molecules that are responsible for the properties of LCPs, located in the side chains. The prepared films based on cellulose derivatives were verified in order to their reflective ability. They also confirmed that the color of light depends on kinetic factors of the solvent removed from mesophase structures. Another example of LLCs was synthesized by [Zhao et al. \(1996\)](#). They studied the copolymers of *n*-hexyl and allyl isocyanates and the length of the formed cross-linking, in which molecules responsible for LCP properties are located in the macromolecular main chain. The authors investigated the orientation of macromolecules regarding the sol fraction, the polymer concentration, and the length of cross-linking. Huge improvements in the mechanical properties of the oriented films were confirmed compared with their unoriented state ([Zhao et al., 1996b](#)). [Alexandridis \(1996\)](#) investigated amphiphilic copolymers and their ability to self-organize. That article focused on copolymers based on poly(propylene oxide) (PPO), poly(ethylene oxide) (PEO), and poly(butylene oxide) (PBO) and the possibility of forming micelles at surfaces and interfaces and also concentrated or in aqueous solutions. For example, triblock copolymer PEO-PPO-PBO can form various lyotropic LC structures, which explains the amphiphilic properties of this copolymer. This characteristic enables various applications of this compound in medicine, the pharmaceutical and agricultural industries, and cosmetics.

3. Rheology of thermotropic liquid crystalline polymers

TLCPs are a class of high-performance engineering thermoplastic polymers with LMW; they offer a balance of properties unequaled by most other resins ([Branch, 2009](#); [Oh et al., 2017](#)). Because of their excellent mechanical properties, high glass temperature, low coefficient of thermal expansion, good dielectric properties, and good resistance to weather conditions, hydrolysis, and gamma radiation, TLCPs are used in many branches of industry and many different applications. Their characteristics are caused by temperature changes ([Qian and Baird, 2016](#)) and depend on the order of liquid crystals. Liquid crystals do not have the three-dimensional order of position of molecules with solid crystals and flow like fluids ([Iwan, 2010](#)). The rheology of LCPs exhibit unique behaviors that arise from complex interactions between crystals and flow. Generally, compared with standard polymers, LCPs have low, and small, or no dye swell during extrusion. To describe the rheological properties of these materials, the equation initially employed for small molecule liquid crystals is used. The equation is also applicable to polymeric liquid crystals, especially in the case of shear flow, as described in [Ahmadzadegan \(2013\)](#). TLCPs are classified into three categories: Types I, II, and III, distinguished from each other

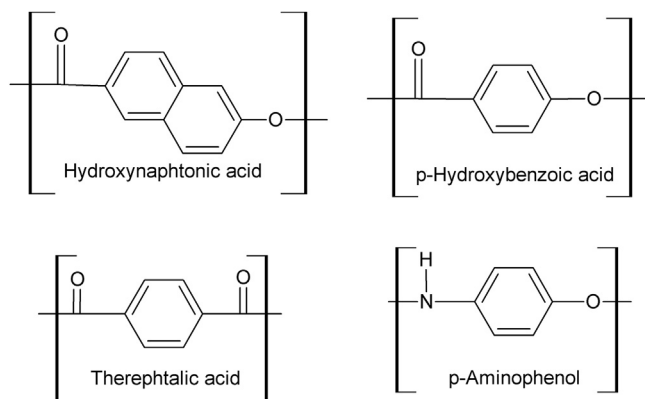
in terms of thermal performance. Types II and III are the easiest to process because they have a relatively low melting temperature and low melt viscosity, which are presented in Fig. 10.8. TLCs Type II are characterized by better mechanical properties compared with Type III (Williams, 1995).

TLCs are commonly formed by heating to a temperature above which the crystal lattice is no longer stable and converting it into an isotropic liquid (without orientational and positional order). For LC materials, the temperature at which melting or phase transition occurs is the melting temperature or crystalline-isotropic transition temperature (T_{C-I}). After cooling, these materials become solid again. TLCs exhibit liquid crystallinity at a well-defined temperature range: between crystalline and LC transition temperature (T_{C-LC}) or at the glass transition temperature for amorphous materials and clearing temperature (T_c). This means that LC materials exhibit one or more intermediate phases and transform from one phase to another and the characteristic temperature for these materials is defined as the crystalline–LC transition temperature. Above that temperature, LCs are an isotropic liquid characterized by temperature T_c . At all of these temperatures, materials at the LC phase are thermodynamically stable (Thakur and Kessler, 2015).

Considering the morphology of TLCs, TLCs are built from two main blocks: rigid (rod-like) and soft (coil-like) (Iwan, 2010). The mesophases of TLCs consist of N, smectic, and cholesteric classes and constitute the basis of rheological properties of these materials. The texture of mesogens should be considered as well during a rheological description of TLCs. In the most cases, above the melting temperature, the long-range order and long-range orientational order occur, but not at the melting temperature, which is short-range and depends on the interaction of neighboring particles (van Krevelen and Nijenhuis, 2009; Rahman, 2013). TLCs are also classified based on the position of mesogenic groups and are divided into two kinds: main chain liquid crystal polymers and side-chain liquid crystal polymers, as described in Subsection 1 (Rahman, 2013).

The main chain of TLC contains mesogenic units directly in the backbone of the molecular chains, whereas in the side-chain TLC mesogenic units link to a polymer backbone. Mesogenic units have the appearance of ellipsoids, but flat and disk shapes have also been observed in TLCs (Rahman, 2013). It is characteristic in the case of thermotropic main-chain LCs that they have a very low melt viscosity with strong temperature dependence compared with other common thermoplastics. This property is especially beneficial in injection molding processing (Li et al., 2012). Rod-like mesogens create a liquid-crystalline phase with a switch such as azomethine, azo, azoxyl, ester, carbonic, or ether groups. Rigid mesogens have aromatic structures, whereas the end groups usually have alkyl, nitrate, alkoxy, cyanic, isocyanic, or halogen (Iwan, 2010). Based on some of these mesogenic groups (Fig. 10.4), thermotropic LC polyurethanes (main chain and side chain) can be obtained (Padmavathy and Srinivasan, 2003).

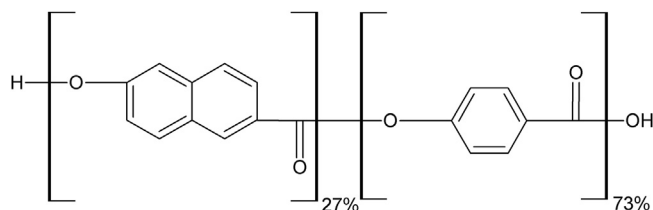
TLCs are usually built from aromatic polyesters or copolyesters characterized by high symmetry in the chemical structure and give extremely high stiffness and strength, yet have sufficient flexibility to melt what is presented in many works

**FIGURE 10.4**

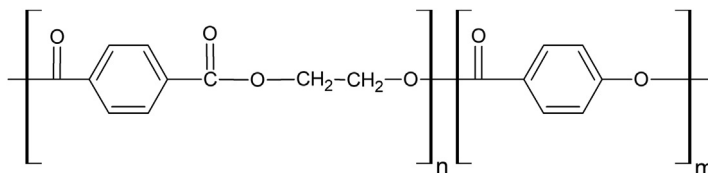
Common functional units of liquid crystalline polymers.

(Driscoll et al., 1991; Gao et al., 1996; Romo-Uribe, 2001; Wilsens et al., 2014a,b; Manurkar et al., 2017). Thermotropic polymers form fibers easily, and even in injection-molded parts, one is immediately struck by the fibrous structure. At the brittle surface, numerous fibrils may be visible (Kiss, 1987). Knowledge about the rheological behavior of these polymers is useful for their further processing (Dealy et al., 1990). Usually thermotropic liquid polymers might be applied as a single component or part of polymer blends with a variety of conventional isotropic polymers (both crystalline and amorphous). The most commonly used and industrial important TCLPs are copolyester of 4-hydroxy-benzoic acid (HBA) and 2-hydroxy-6-naphthoic acid, well-known as Vectra A950 and Vectran, and shown in Fig. 10.5. Next are X7G: copolyester of *p*-hydroxybenzoic acid (p-HBA) and ethylene terephthalate (Fig. 10.6) and Xydar: *tert*-polyester of p-HBA; *p,p'*-biphenol, and terephthalic acid (Fig. 10.7) which have higher thermal stability compared with Vectra. Other interesting examples of TLCPs are copolyesteramide of 2,6-hydroxynaphthoic acid, terephthalic acid, and aminophenol; and copolyester of 2,6-hydroxynaphthoic acid, terephthalic acid, and hydroquinone.

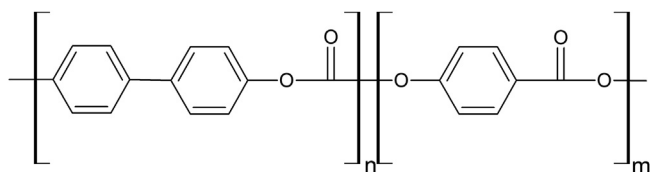
If we consider the effect of the complex structure of the copolyester described in the literature, HBA/polyethylene terephthalate (PET) (80/20), we find that at the melt temperature next to an N melt phase are crystalline phase and nonlayered periodic crystals owing to a three-phase system consisting of a mixture of N liquid crystal and solid, as described by Yu et al. (2007). The fast initial relaxation occurs after cessation of flow which is independent on used shear rate. During the first part of relaxation, local molecular rearrangements occur, whereas the second part of relaxation involves the director profile. The relaxation rate of shear stress depends on the contributed shear rate during shear flow. Yu et al. examined a thermotropic LC copolymer of 80 mol.% *para*-hydroxybenzoic acid and 20% poly(ethylene terephthalate) (LC-5000) in terms of its rheological properties and relaxation process. To determine the rheological properties of the copolymer, dynamic and creep

**FIGURE 10.5**

Example of copolyester Vectra A950 of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid as a thermotropic liquid crystalline polymer.

**FIGURE 10.6**

X7G: copolyester of *p*-hydroxybenzoic acid and ethylene terephthalate as a thermotropic, nematic liquid crystalline polymer.

**FIGURE 10.7**

Xydar: *tert*-polyester of *p*-hydroxybenzoic acid; *p,p'*-biphenol and terephthalic acid as a thermotropic liquid crystalline polymer.

experiments were conducted. Based on the results, it was noted that the storage modulus (G') and loss modulus (G'') decreased with an increase in temperature and showed a change in slope at about 294–2958°C (Yu et al., 2007). The TLCP molecules gradually lost the long-range order of position at the melting temperature of the solid crystal part (about 270°C) and retained the short-range order of orientation. LC-5000 was characterized by small creep compliance ($<0.1 \text{ Pa}^{-1}$); the compliance plateau for that copolymer was recorded at 280°C, which is characteristic of solid-like behavior. The relaxation behaviors of LC-5000 in the melting interval were greatly influenced by the solid crystals. The relaxation time of chain orientation and deformed polydomains depended on the temperature (Yu et al., 2007).

Fan et al. studied the dynamic viscosities of five commercially available TLCPs: 1712 (Sumikasuper E6807LHF), 1741 (Titan LG441), 1746 (Vectra T840), 1768 (VENO LCP 2030G), and 1769 (VENO LCP 6040GM). They indicated that all TLCP materials exhibited a typical shear-thinning behavior obeying the power

law with power indices from 0.2 to 0.3. Based on the results, the dynamic viscosities first rapidly decreased by two to three orders of magnitude, because these TLCPs are heated above the melting temperatures; then, the viscosities level off and gradually increase with a further increase in temperature (Fan et al., 2003).

Many researchers have extensively studied copolyesters. One example of the application of thermotropic main chain LCP was to enhance melt-state reactive processing with triphenyl phosphite, which can react with up to three polymer chain ends through their chain end functionalities (Li et al., 2012). Another example of their use is to prepare ternary blends of polyarylate U-Polymer 100 and block copolyester ether Hytrel 7246 (Hong and Kim, 1994). TLCPs exhibit interesting properties; they contain nanofillers. Chow et al. (Chow et al., 1993; Drappel et al., 1997) investigated TLCP copolyesters based on poly(methyl methacrylate), which had an N mesophase after achieving a temperature of 48°C. Moreover, they investigated the impact of two types of plasticizers and solvent on the morphology and rheology of prepared solvent cast films based on TLCPs. Results verified that the synthesized solvent cast films showed solvent-induced crystallization. Furthermore, the addition of plasticizer did not affect the temperature in which the N mesophase formed, but it affected the morphology and rheology of the prepared TLCPs. The researchers also investigated changes in the composition of TLCPs with nanomaterials or in blends with different kinds of TLCPs. There has been increasing interest in investigating nanocomposites and blends based on various types of LCPs. The impact of different LCP matrices, LCP concentrations in blends, amounts and kinds of nanofillers, etc., on the morphology, thermal and mechanical properties, and, sometimes the rheology of LCP-based polymer materials have been studied. Kim (2009) investigated the reinforcing effect of carbon nanotubes on TLCP-based nanocomposites. The TLCP matrix was formed by copolyester synthesized using poly(*p*-hydroxybenzoate) and poly(ethylene terephthalate) at a ratio of 4:1, respectively. Carbon nanotubes were added at 0.5, 1.0, and 1.5 wt.%. Results indicated that the best interfacial interaction between the carbon nanotubes and TLCP matrix were the nanocomposite with the lowest amount of nanofiller, which had the best mechanical properties of the nanocomposites. Vivek et al. (2017) also studied nanocomposites based on TLCPs and carbon nanotubes. A TLCP matrix was used as a copolyester of 4-hydroxybenzoic acid and 6-hydroxy-2-naphtoic acid at a molar ratio at 73:27, respectively. The carbon nanotube concentration was 0.5–5 wt.%. The mechanical properties for these type of nanocomposites indicated an increase in the modulus and hardness with an increase in the amount of nanofiller. Both articles confirmed the impact of the TLCP matrix structure on the mechanical properties of the resulting nanocomposites. Meng et al. (2017) investigated the effect of different dimensional carbon nanoparticles on the shape memory behavior of TLCP-based nanocomposites. A poly(4,4'-bis[6-hydroxyhexyloxy]biphenyl phenyl-succinate) TLCP matrix was used. The nanoparticles used were used fullerene, carbon nanotubes, and graphene. The results confirmed the negative effect of the added carbon nanoparticles on shape memory behavior, but all fillers enhanced the mechanical properties of the prepared materials.

In the case of polymer blends, TLCPs combine miscible or immiscible blends with other polymers. Adding a small amount of a TLCP to a polymer blend is

advantageous because its low melt viscosity can reduce the melt viscosity of polymer blends, simplifying processing. What is more, if the TLCP is used at a small amount, it forms highly elongated domains parallel to the direction of flow. That is why blending TLCPs with other thermoplastics has become an interesting subject of many works. Because of the high degree of molecular order in the melt state, TLCPs can create fibrils, which constitute a reinforcement component for the thermoplastics matrix. TLCP fibrillation in a thermoplastic melt is a complex process that depends on miscibility and immiscibility between TLCPs and the thermoplastic matrix, the content of TLCPs, the viscosity ratio of the TLCP to the matrix, the processing temperature, the processing history, and the shear and elongational flows. The application of TLCPs as reinforcements are common in the practice of filling thermoplastic polymers because reinforcing components are derived during processing (usually molding or extrusion) (Kiss, 1987; Qiao et al., 2001; Branch, 2009). Next to injection molding and extrusion, the low viscosity of TLCPs is used in the spin process, which is simulated with steady-state boundary conditions imposed at fixed upstream and downstream locations (Forest et al., 1999). For polymer blends based on immiscible TLCPs and thermoplastic polymers, their properties depend on the ratio of the two components and the viscosity ratio is the characteristic physical property. The ratio is the result of the molecular weight of the thermoplastic polymers and the melt processing temperature. Various morphologies with the same two immiscible polymers have been noted (Demeuse, 2014).

Determination of rheological characteristics including viscosity, the flow share rate, and viscosity curves (at a changing share rate) of TLCPs have an important role in predicting their behavior during various processing methods such injection molding, extrusion, or spinning, during which shear forces at different rates of shear are applied. Fig. 10.8 presents the viscosity—shear curve of anisotropic and isotropic

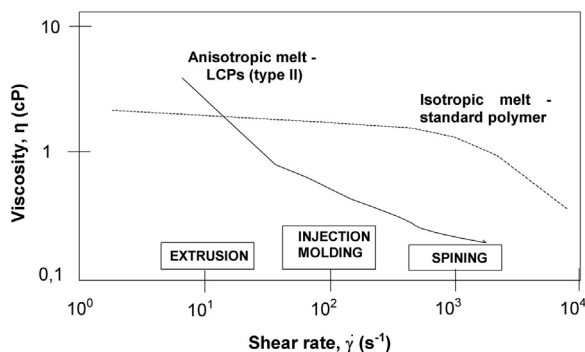


FIGURE 10.8

Viscosity—shear curve of anisotropic and isotropic melts: liquid crystalline polymer (LCP) Type II and conventional polymer melt.

The scheme was prepared by Authors based on Williams, G.E., 1995. Chapter 7: Thermotropic liquid crystal polymers in Editors: Chilton, J.A., Goosey, M. In: *Special Polymers For Electronics And Optoelectronics*, 1st edition. Springer Science+Business Media Dordrecht. <https://doi.org/10.1007/978-94-011-0569-9>.

melts compared with conventional and unconventional ones (LCPs, Type II) (Williams, 1995).

The rheological properties of thermotropic liquid crystal polymers strongly depend on the temperature and can be determined in theoretical and experimental ways. Unfortunately, analysis is difficult compared with other types of LCPs, not to mention standard liquids. Determination of the viscosity of TLCPs at a steady shear flow is exploitable to determine not only the non-Newtonian flow of the melt, but also the performance of the extruder, shear thinning characteristics, or stable melt flow during stretching (Ahmadzadegan, 2013). Concerning the rheological parameters of TLCP, in addition to their type, the texture of mesogenic units also have an important role. Moreover, the position of mesogenic units at the chain of TLCP provide complex viscosity. Molecules of thermotropic liquid crystals might be oriented by electromagnetic fields and mechanical stress or shear. This orientation affects their melt viscosity (Rahman, 2013). To understand the rheological behavior of LCPs fully, often it is necessary to use various structure-probing techniques to study their molecular and supermolecular structural levels. These techniques include microscopic, rheological, rheoptical, and small angle light scattering, small angle neutron scattering, and small angle x-ray scattering (Jan Mewis and Moldenaers, 1996).

Based on the literature, it was found that different shear rate regions are for different types of orientation. Many scientific works corresponding to rheological characteristic of TLCPs were conducted for materials with an N structure because of the possibility of their wide-ranging application and easy processing. The rigid rod-like molecules rotate on their own axis, known as tumbling. The range of shear rates that the melt experiences in an extruder can be determined from steady shear rheology. In the low shear rate region, viscosity decreases with an increase in the temperature; hence, low energy is required to processing the easily oriented rod-like molecules of LCPs. If the temperature is higher, above the melting point and at the intermediate shear rate region, some portion of N molecules is transformed to the isotropic phase and N–isotropic transition occurs with a simultaneous increase in shear viscosity. A further increase in temperature brings a decrease in viscosity (Ahmadzadegan, 2013; Rahman, 2013).

The rheological behavior of typical liquids can be described by mathematical models for both Newtonian and Non-Newtonian fluids. In the case of LCPs, the situation becomes complicated. There is no one best theory that can be used to describe these materials. Each type is different in the mesogenic group. The position and texture of TLCPs should be considered individually. However, LCPs reveal a certain similarity in behavior with that of LMW liquid crystals (Shibaev and Plate, 1984), which is why the continuum mechanics approach was based on the Leslie–Ericksen theory for LMW liquid crystals and the molecular theory initially developed by Doi, Hess, and Semenov is used to describe LCP rheology. These theories can be applied to defect-free samples, but LCPs usually exhibit defects or have domains that are rheologically important but extremely difficult to model (Jan Mewis and Moldenaers, 1996). Nevertheless, considering the low

shear rate region, the theoretical prediction of viscosity from Doi theory correlates well with experimental data. The rheological behavior of LCPs is known to depend on the nature and on the mesophase texture. The initial Doi theory, express by Smoluchowski, is given in Eq. (10.3). This equation is used to characterize the molecular dynamics of the rigid rod-shaped molecule (Larson and Mead, 1991):

$$\frac{\partial \Psi}{\partial t} + \frac{\partial}{\partial \tilde{\mathbf{u}}} \cdot \left[\left(\tilde{\mathbf{u}} \cdot \tilde{\nabla} \mathbf{v} - \tilde{\mathbf{u}} \tilde{\mathbf{u}} \tilde{\mathbf{u}} : \tilde{\nabla} \mathbf{v} \right) \Psi \right] - \frac{\partial}{\partial \tilde{\mathbf{u}}} \cdot \hat{D}_r \left(\tilde{\mathbf{u}} \right) \left[\frac{\partial \Psi}{\partial u} + \Psi \frac{\partial}{\partial \tilde{\mathbf{u}}} \left(\frac{V_{ev}}{kT} \right) \right] = 0 \quad (10.3)$$

where ψ = the probability that a rod has an orientation given by the unit vector $\mathbf{u}$; $\tilde{\nabla} \mathbf{v}$ = the velocity gradient; $\frac{\partial}{\partial \tilde{\mathbf{u}}}$ = gradient operator on the unit sphere; $\hat{D}_r \left(\tilde{\mathbf{u}} \right)$ - orientation = the depended rotary diffusivity; and V_{ev} = the effective excluded-volume potential.

The three-region viscosity curve (Fig. 10.9) proposed by Onogi and Asada is often used to consider thermotropic liquid crystal polymer rheology (Dealy et al., 1990; Jigounov, 2007). At Regions I and III, at the range of the low and high shear, rate the viscosity is shear thinning. At Region II the region of the Newtonian plateau is assigned.

It is worth to mention that the relative values of melt viscosities depend on the composition of copolymers which usually consist of mesogenic and nonmesogenic units (Ahmadzadegan, 2013). Alternative approaches to develop rheological constitutive equations for LCPs is the Poisson-Bracket method which is potentially

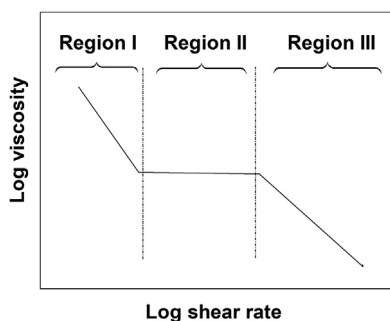


FIGURE 10.9

The three-region logarithmic viscosity curve of thermotropic liquid crystalline polymers scheme based on the by Onogi and Asada theory.

The scheme was adapted from Onogi, S., Asada, T., 1980. Rheology and rheo-optics of polymer liquid crystals. Rheology, Springer, Boston, MA, pp. 127–147.

appropriate for complex systems like for mentioned materials (Jan Mewis and Moldenaers, 1996).

Depends on the shear flow the Larson and Doi theory for mesoscopic domains is applied. This theory provides a plausible description for the evolution of the defect density (or domain size) under shear flow for a defect-laden polymeric fluid. The equation according to this theory can be considered only to the intermediate shear rate region (region II – Fig. 10.9). To describe the region I (as well as region II) the modified the Larson-Doi Eq. (10.4) can be used to low shear rate region (Kim et al., 1997):

$$\frac{dL}{dt} = \alpha \dot{\gamma} L - \beta \frac{K}{\eta} (L - L_0)^2 \text{ or } \frac{d(a^2)}{dt} = \beta \frac{K}{\eta} \left(1 - \frac{a^2}{a_0^2}\right)^2 - \alpha \dot{\gamma} a^2 \quad (10.4)$$

where L or a^{-2} = the defect density; L_0 = the initial defect density; a_0 = initial domain size; α and β = dimensionless constants, keeping a typical rule of the Ericksen number Er , $\sim 13/tz-100$.

According to the modified the Larson–Doi equation the steady shear viscosity indicates the shear thinning behavior at low shear rates, reflecting the domain flow with a decrease in size or the effect of the initial texture on the preparation (Kim et al., 1997).

For technical aspects of rheological measurements on TLCPs, these measurements are difficult because of a few complication during investigation (e.g., outgassing or interrelations caused by long stress transients during startup in viscosity measurements in capillaries). Measurements for this kind of LCP are taken using instruments such as capillary rheometers. Nonlinear Bagley plots have been reported for LCPs including different factors such nonuniform temperature distribution over the channel; wall effects such as wall slip can also cause deviations from linearity, reducing the shear rate and the slip velocity changing with pressure. Practical applications of Bagley plots have found in extrusion processing because of pressure effects generally considered to be an ascendant effect (Moldenaers et al., 1996).

In the literature are works related to the model for rheological investigations of fiber spinning of TLCPs which couple hydrodynamics, anisotropic rod-like microstructural dynamics, free surface effects, and thermodynamics. The model incorporates a Doi-type theory for nematodynamics, along with physical constants, empirical correlations for air drag and functional heat loss coefficients, and rheological relations consistent with the melt processing of TLCPs, as fully described in Forest et al. (1999).

4. Conclusion

LCPs are versatile compounds with excellent optic, mechanical, and electrical properties. They are leading the technology in optics, electronics, motorization, medical devices, and pharmacy. Knowledge of the rheological behavior of LCPs,

which is related to their chemical structure, including their chemical nature and the kind of mesogenic units, rigid or flexible, and their orientation along the main chain, have a crucial impact on further processing methods. This information about the rheological parameters and chemical structure is data input to for modeling processing such injection molding, extrusion, or spinning of LCPs. Many research papers and chapters are devoted to LCPs describing these materials according to their structure and morphology and their chosen properties including their rheology. This group of polymeric materials cannot be described by a single perfect fitted theory of rheological behavior. On the one hand, the anisotropic nature of LCPs the stress-shear hinders the characterization of LCPs, but it also lead to achieving unique properties of materials. High hopes of developing LCP materials related to nanomaterials especially dedicated to the medicine and pharmacy industries. This may be a platform for smart materials.

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Rheo-SAS: feasibility to characterize concentrated colloidal particle suspensions for their processing

11

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Abstract

This chapter summarizes the series of different developments and investigations on in situ coupling of rheology with small-angle scattering (rheo-SAS) measurements of colloidal particle suspensions. This coupling allows us to directly correlate microscopic particle–particle interaction with macroscopic suspension behavior under different physical and chemical environments. This summary provides a better understanding of the basic phenomena/theory associated, historical development and current status of rheo-SAS, and also discusses its applicability and limitations/variations to different types of concentrated particle suspensions. Two different rheo-SAS methodologies, i.e., rheo-SAXS (small-angle X-ray scattering) and rheo-SANS (small-angle neutron scattering), are introduced and discussed in terms of their similarities/differences as well as strength/uniqueness. In this article, aqueous suspensions composed of colloidal particles, including metal oxide particles and their composites with clay particles and polymers, are introduced as examples. The research gaps are identified and specific future perspectives are discussed to further enhance the use of this useful coupling, and its application toward the transition from the evaluation of simple particle suspension systems to more complex particle suspension systems that fit more with the interest and needs of particle processing industries.

Keywords: Complex particle system; Concentrated suspension; Particle–particle interaction; Small-angle neutron scattering; Small-angle X-ray scattering; Zeta potential.

1. Introduction

There are different complementary methods with rheological measurements (e.g., scattering, imaging), in terms of enhancing our understanding of microscopic particle–particle interactions that can explain the macroscopic particle suspension

rheological behaviors. In the following sections, scattering methods that have found very good features to couple with suspension rheological properties will be introduced and discussed.

Scattering reflects the shape and size of scatters (e.g., colloidal particles), as well as the scattering contrast and volume, characteristic lengths, and the surface area to volume ratio (Anovitz and Cole, 2015). Those information can be modified with changing the microscopic interaction between particles within a suspension/dispersion that can change macroscopic behavior, such as an increase suspension viscosity/yield stress that is a useful factor to formulate and manipulate a colloidal product (Otsuki and Bryant, 2015).

In a neutron diffraction/scattering experiment, the measured differential cross-section $d\Sigma/d\Omega$ can be composed of two different contributions as follows (Anovitz and Cole, 2015):

$$\frac{d\Sigma}{d\Omega} \propto b^2 \left| \sum_i e^{-iq \cdot r_i} \right|^2 + N \left(\langle b^2 \rangle - \langle b \rangle^2 \right) \quad (11.1)$$

The first contributor, called coherent scattering, provides the information about the structure of the material, i.e., the relative distances between atoms in a sample and as a superposition of the scattering waves creating the amplitude of the angle-dependent intense coherent scattering at low q range. On the other hand, the second contributor, incoherent scattering carries no information about the relative distances between atoms in the sample; but background-like weak flat scattering wave without angle dependent at high q range (Anovitz and Cole, 2015).

For a group of identical, randomly oriented particles, the intensity of coherent, elastic scattering is dependent only on the magnitude of the scattering momentum transfer q and is defined as follows (Anovitz and Cole, 2015):

$$I(q) = N(\Delta\overline{SLD}V)^2 P(q)S(q) \quad (11.2)$$

N is the number of particles per unit volume, V is the volume of the particles, $P(q)$ is a form factor that depends on the shape of the particles, $S(q)$ is a structure factor that dictates the interparticle correlation structure, and $\Delta\overline{SLD}$ is the scattering length density difference between the scattering particles and solvent.

The above relationship can be reduced to Eq. 11.3 or 11.4:

$$I(q) \propto (\Delta\overline{SLD} \cdot V)^2 \quad (11.3)$$

$$\text{Or } \pm \sqrt{I(q)} \propto (\Delta\overline{SLD} \cdot V) \quad (11.4)$$

Fig. 11.1 describes their relationship and indicates the presence of match point where $I(q)$ or $\sqrt{I(q)}$ is equal to zero. In other words, the scattering intensity becomes zero. This aspect and the usefulness of contrast variation will be further discussed in Section 3.

This article introduces the theory of scattering as well as complementarities with suspension rheology and then discusses the characterization methods focusing on

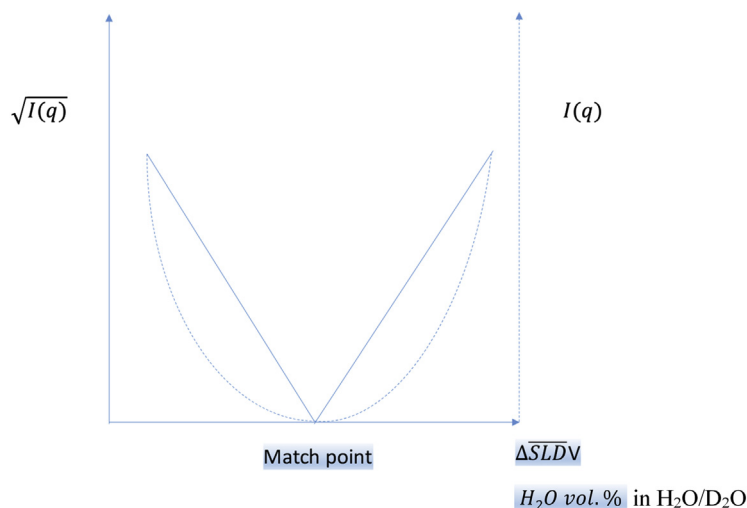


FIGURE 11.1

Contrast match concept, showing the $\sqrt{I(q)}$ and $I(q)$ as a function of $(\Delta SLD \cdot V)$ or H_2O vol. % in H_2O/D_2O .

rheo-SAS to explain microscopic particle–particle interactions as well as macroscopic suspension behaviors.

Thus, the specific aims of this paper are as follows:

- *To review the basic theory and phenomena involved, historical development and current status of rheo-SAS as the characterization methods of concentrated colloid dispersions/suspensions;*
- *To review its applicability and limitation to evaluate the linkage between particle–particle interactions and macroscopic suspension behaviors in a concentrated colloidal dispersion/suspension;*
- *To focus on reviewing the previous works on the rheo-SAS measurements of colloid dispersions/suspensions to summarize the state-of-arts as well as the research gaps; and*
- *To provide the detail future perspectives one can take over to enhance our understanding and characterization of the concentrated colloid dispersion/suspension and improve their formulation and manipulation.*

Within the above frameworks, scattering theory is first revisited, followed by the review of application of rheo-SAS measurements to characterize colloid dispersions/suspensions in terms of historical advancement and recent development toward the discussion on characterization of more complex colloid systems, including polydisperse colloidal particle systems. The details of each component will be explained more in the following sections. Other relevant topics, such as the yield stress determination, and coupling other physicochemical properties (e.g., zeta

potential) with the DLVO forces are out of the focus of this chapter. Some insights for such topics can be found in the papers written by [Nguyen et al. \(2006\)](#) and [Otsuki \(2018\)](#) respectively.

2. Rheo-SAS and its application to colloid systems

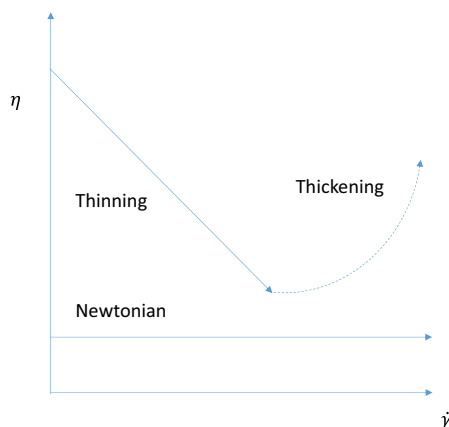
Suspension rheology reflects the microscopic interaction between particles within a suspension/dispersion and shows the change in macroscopic behavior, such as an increase in the viscosity and/or yield stress due to the stronger particle interactions. Change in the viscosity can affect the process ability of a particle suspension/dispersion and thus process yield. The lower the viscosity by diluting a suspension, the higher the transportability; but less amount of particles can be processed. On the other hand, increasing the particle concentration would increase the particle–particle interaction and the viscosity, and thus lower the transportability and could result in the less process yield. In addition, so-called rheology modifiers can be used to maintain a reasonable process yield in many industrial applications, including mining, paintings, (e.g., [Chana et al., 2007](#)). Apparently, many industries dealing particle suspension/dispersion systems are interested in increasing the particle/solid concentration to aim for a higher productivity as well as the effective waste/tailings management ([Boger, 2009](#)).

Understanding the suspension rheology is one of the key tasks for someone who deals with concentrated colloidal particle suspensions/dispersions, to properly maintain and manipulate the process ability, and thus achieve a good yield of his/her products through a proper suspension/dispersion processing. In situ scattering measurements under the shear application can help us understand the effect of shear on microscopic particle–particle interactions and thus macroscopic suspension rheology.

2.1 Shear thickening

Shear thickening increases suspension viscosity with increasing shear rate above its certain threshold value below that the viscosity decreases ([Fig. 11.2](#)). On the other hand, the majority of non-Newtonian fluids behaves so-called shear thinning that decreases the suspension viscosity with increasing shear rate (e.g., [Bergstrom, 1998](#)).

There are several well-known shear thickening fluids, including corn starch suspension (e.g., [White et al., 2009](#); [Saint-Michel et al., 2018](#); [Brown and Jaeger., 2014](#); [Madraki et al., 2017](#)) and silica particle suspensions (e.g., [Brown and Jaeger., 2014](#); [Maranzano and Wagner, 2002](#)). In the later section, silica particle suspension showing shear thickening behavior will be introduced with the aim of introducing rheo-SANS (small-angle neutron scattering) application to study shear thickening suspension. Shear thickening has been explained by many different mechanisms, including the hydroclustering of colloidal size particles (e.g., [Madraki et al., 2017](#); [Bender and Wagner, 1995, 1996](#); [Phung and Brady, 1996](#); [Melrose et al., 1996](#); [Farr et al., 1997](#); [Brady and Bossis, 1988](#)).

**FIGURE 11.2**

Viscosity as a function of shear rate of three different types of suspension, i.e., Newtonian, shear thinning, and shear thickening.

3. Scattering of colloidal systems

Scattering is one of the most proven methods to characterize colloidal particle dispersions/suspensions. As stated in the introduction and the following sections, understanding the dispersion/aggregation state of colloid suspension systems is significantly important to properly handle and manipulate them to formulate the products with desired physical and chemical properties. To achieve that, characterization by scattering methods is a powerful tool because they can help us understand the particle dynamics and stability of colloidal systems through change in size and structure of particles/aggregates under different physical and chemical environments. Among the scattering methods, here we focus on the small-angle scattering method, especially SANS and its family in terms of theories and methodologies relevant to the colloid systems.

Let us first define the size range of our interest in colloid systems. Fig. 11.3 (Lopez-Rubio and Gilbert, 2009) shows the multiscale association with the formation of starch from atomic structure to microstructure, in the order of 10^{-11} to 10^{-3} m that should be characterized by the application of different methods. Among them, SANS can probe the nanostructures from 10^{-9} to 10^{-7} m, while the ultrasmall-angle scattering allows us to measure microstructure in the order of 10^{-7} to 10^{-5} m where similar size range can be characterized by the other method, so-called spin-echo small-angle neutron scattering (SESANS) (e.g., Bouwman et al., 2011; Andersson et al., 2008a, 2008b; Bota et al., 2007; Krouglov et al., 2003; Trompa and Bouwman, 2007), ultrasmall-angle neutron scattering e.g., (Rehm et al., 2013; Kwaambwa et al., 2017; Agamalian et al., 1997, 2018;

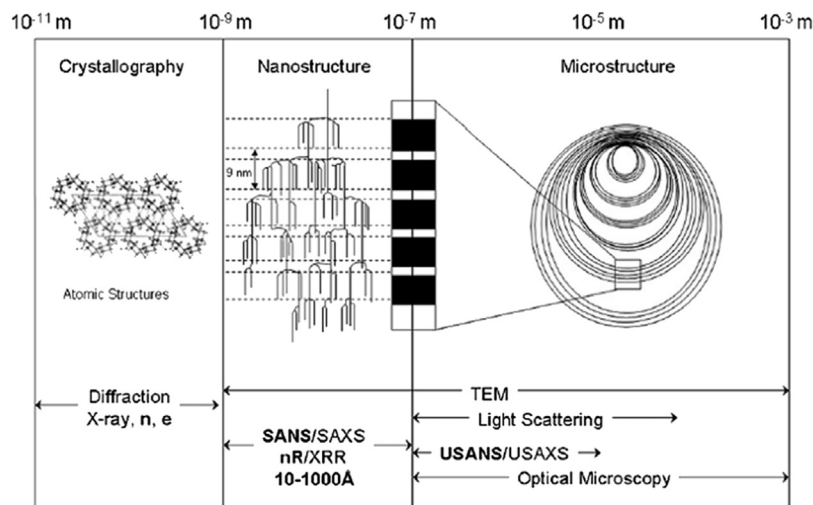


FIGURE 11.3

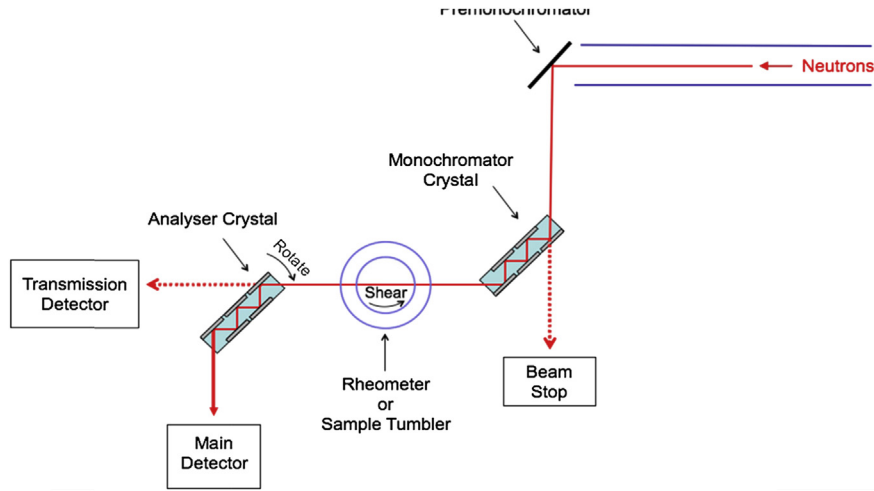
Correlation between structures and the characterization method selection (Lopez-Rubio and Gilbert, 2009).

Ebrahimi et al., 2010; Freund and Rehm, 2014; Hainbuchner et al., 2000), and very small-angle neutron scattering (e.g., Zentrum, 2015; Vogtt et al., 2014). Apparently, nanostructures determine microstructures that reflect the macroscopic behavior (e.g., rheology) of a colloid dispersion/suspension. Understanding such tiny structures will help us explain the macroscopic behavior and the mechanisms behind those structuring.

In neutron scattering beamlines, in situ rheological measurement is one of the popular setups, to capture both microscopic particle–particle interactions and macroscopic suspension behavior. Fig. 11.4 shows a setup can be available for a user measurement in KKB USANS beamline in ANSTO, Australia (Otsuki et al., 2018). Rheometer flow cell applies the shear to a sample inside while scattering measurement can be made during the shear. The most common rheometer geometry in such a rheo-SAS setup is the bob and cup geometry.

Neutron is sensitive to small atoms, while X-ray is not; but the more intense beam can be accessible. Table 11.1 shows the typical comparison between the neutron and X-ray as a source of characterization tool. Access to the facility to perform rheo-SAS experiment can be very limited, in terms of high competition and limited number of days; usually competition is very tough.

One of the major advantages of SANS and their relevant methods is utilization of contrast variation to scatter the objectives (often called scatterer) of your interest and/or minimize the scattering of the other objectives of noninterest, by varying the ratio between $\text{H}_2\text{O}/\text{D}_2\text{O}$ in a system. As stated in the introduction, different atoms scatter differently. It can be characterized by using the values, so-called

**FIGURE 11.4**

Rheo-USANS setup in KKB beamline at ANSTO (Otsuki et al., 2018).

Table 11.1 Comparison between neutron and X-ray characteristics in terms of their utilization as a source of material characterization tool.

	Neutron	X-ray
Detection of small atoms	Yes	No
Brightness	Low (depends on the source)	High
Laboratory source	Rare	Yes

scattering length and cross section while the average feature as a compound is characterized by the average scattering length density given by (Anovitz and Cole, 2015)

$$SLD = \frac{\sum_{i=1}^n x b_{c(i)}}{V_m} \quad (11.5)$$

where $b_{c(i)}$ is the bound coherent scattering length of the i th n atoms in the compound, and V_m is the molecular volume given by

$$V_m = \frac{m}{N_A \rho} \quad (11.6)$$

where m is the molecular mass of the phase, N_A is the Avogadro's number, and ρ is the phase density.

Table 11.2 (Lopez-Rubio and Gilbert, 2009) shows the neutron and X-ray scattering lengths and cross sections for food colloid relevant elements and indicates their differences and features.

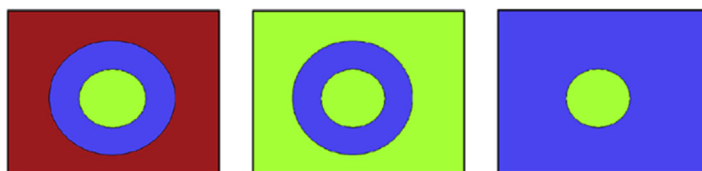
Fig. 11.5 indicates the H_2O/D_2O contrast variation can reveal the information of interest part of a sample while it can hide the information of no interest, or

Table 11.2 Neutron and X-ray scattering lengths and cross section^a for food relevant elements (Lopez-Rubio and Gilbert, 2009).

Atom	Nucleus	$b_{\text{coh}} (10^{-12} \text{ cm})$	$\sigma_{\text{coh}} (10^{-24} \text{ cm}^2)$	$\sigma_{\text{incoh}} (10^{-24} \text{ cm}^2)$	$b_{\text{x-ray}} (10^{-12} \text{ cm})$
Hydrogen	^1H	−0.374	1.76	79.7	0.28
Deuterium	^2H	0.667	5.59	2.01	0.28
Carbon	^{12}C	0.665	5.56	0	1.69
Nitrogen	^{14}C	0.940	11.1	0	1.97
Oxygen	^{16}C	0.580	4.23	0	2.25
Phosphorus	^{31}P	0.517	3.31	80	4.22
Sulfur	$^{32}\text{S}^a$	0.285	1.02	0	4.51

coh = coherent; *incoh* = incoherent. A scattering length, b_p , is associated with a cross section such that $\sigma_i = 4\pi b_i^2$.

^a Natural abundance 95%.

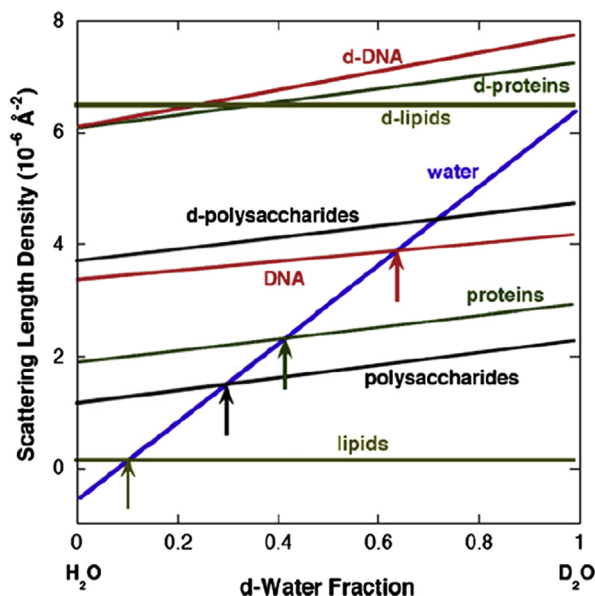
**FIGURE 11.5**

The concept of contrast matching to investigate the multicomponents/ingredients systems. A core-shell nanostructure is given as an example (Lopez-Rubio and Gilbert, 2009).

selectively extract information one-by-one. To visualize the core, one can assign the scattering length density of solvent to be same/similar as its shell value, while for investigating the shell, one should give the same/similar values between the core and the solvent. With tuning the different scattering length density between the solvent and core/shell, we can see the properties/behavior of two different components. Scattering length density of the system can be calculated by using Eq. (11.5) with varying the $\text{H}_2\text{O}/\text{D}_2\text{O}$ ratio.

Contrast variation can also be used to reduce the effects of multiple scattering (Otsuki et al., 2018) that is one of the most difficult challenges in scattering measurements of concentrated particle suspensions (e.g., Anovitz and Cole, 2015; Otsuki et al., 2018; Vineyard, 1954; Sabine and Bertram, 1999; Connolly et al., 2006).

Fig. 11.6 (Lopez-Rubio and Gilbert, 2009) also visualizes how to identify the match point by calculating and plotting the scattering length density as a function

**FIGURE 11.6**

Scattering length density of common food components as a function of the water volume fraction in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mix (Lopez-Rubio and Gilbert, 2009).

of volume fraction of water in H₂O/D₂O mix. Arrows indicate the match point with different food-based material systems. As shown in this figure, the match points can be varied significantly with different materials of interest. Thus, it is highly recommended to know the match point of your food ingredients and focus on which of them you wish to investigate through SANS measurements and data analyses.

4. Rheo-SANS case study

4.1 Rheo-SANS: feasibility to characterize concentrated polydisperse colloidal particle suspensions

This section reports the series of investigations on in situ coupling of rheology with small-angle scattering (rheo-SAS) measurements of colloidal particle suspensions (e.g., Otsuki, 2019). This coupling allows us to directly correlate microscopic particle–particle interactions with macroscopic suspension behavior under different physical and chemical environments. In this section, some results obtained with aqueous suspensions composed of colloidal particles, including polydisperse silica particles, are introduced as examples, measured by Rheo-SANS. The research gaps are identified and specific future perspectives are discussed to further enhance the use of this useful coupling, and its application towards the transition from the evaluation of simple particle suspension systems to more complex particle suspension systems that fit more with the interest and needs of particle processing industries.

4.1.1 Background of the case study

Proper characterization of concentrated colloidal particle suspensions is still a challenging task because majority of characterization methods usually require a dilute suspension whose analysis could overlook potential issues associated with enhanced particle–particle interactions leading to particle coagulations and thus increasing suspension viscosity and facing difficulty in handling such a suspension (e.g., Otsuki and Bryant, 2015). Understanding the correlation between macroscopic flow behavior and microscopic physicochemical properties of concentrated colloidal particle suspensions is thus very important. Characterization research coupling those two aspects towards the enhancement of process and application of a *concentrated* colloidal suspension is thus highly encouraged (e.g., Otsuki, 2018).

One of them can be coupling suspension rheology and colloidal forces to further understand the influence of microscopic particle–particle interactions on the macroscopic suspension behavior under different chemical environments. Such correlation has been reported in many different aspects (e.g., Franks et al., 2000), while there are so many research gaps even in a focused area of this coupling, e.g., utilization of suspension yield stress (Otsuki, 2018). At the same time, understanding the macroscopic behavior of a concentrated suspension is of great importance in scientific and engineering point of views because processing and application of colloidal particle suspensions are vital of our modern society, including daily life products (e.g., food, cosmetics) and advanced technologies (e.g., batteries).

This section reports our attempt (Otsuki, 2019) to couple microscopic particle interactions with macroscopic suspension rheology with quartz and corn starch

aqueous suspensions as examples. Shear thickening fluid is an example of non-Newtonian fluid which exhibits the increase in viscosity with the rate of shear strain. This shear thickening behavior can be observed in various dispersions/suspensions, including metal oxide particle (e.g., Mewis and Wagner, 2012) and corn starch (e.g., Fall et al., 2012). This behavior can be explained by the hydrocluster formation of particles under high shear rate. The microstructure change through scattering patterns obtained from rheo-SANS experiment with monodisperse nanoparticle systems (e.g., silica particles) was reported to explain the shear thickening behavior (e.g., Mewis and Wagner, 2012). On the other hand, the polydisperse micronsize particle dispersion systems have been rarely studied/reported possibly due to the limitation of accessible q -range and the weak signals from their hydrocluster formation. In this study, we aimed to develop a rheo-VSANS method to address the above issues using a VSANS beamline to access the lower q -range and the higher flux. This investigation is of not only the great scientific interest but also practical interest to understand and properly manipulate particles and their dispersion behaviors in industrial application because plant operations often deal with polydisperse micronsize particles to yield final product.

In 2016 (e.g., Otsuki, unpublished results), we confirmed the presence of correlation peaks from the scattering intensity versus q plot of our silica dispersion samples prepared in different D_2O/H_2O ratio in a VSANS beamline. In addition, the shear thickening behavior of silica dispersion under a specific condition in terms of pH and solid concentration was observed in two different geometries, i.e., Couette and cone plate (Fig. 11.7) (Otsuki et al., 2019).

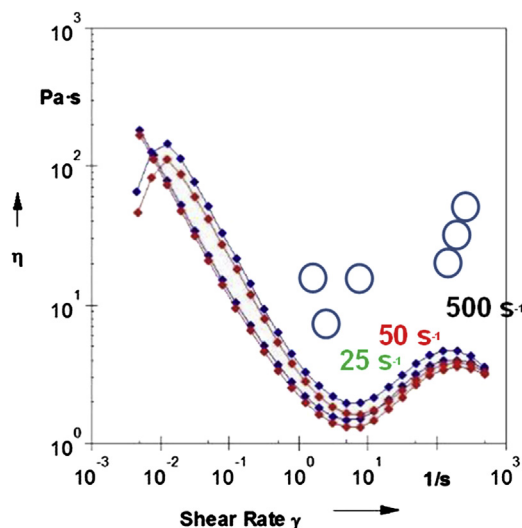


FIGURE 11.7

Viscosity of micronsize silica particle dispersion in glycerol/water mix as a function of shear rate.

Modified from Otsuki, A., June 2019. Rheo-SAS: feasibility to characterize concentrated colloidal particle suspensions for their processing. Proc. European Metallurgical Conference 2019, Dusseldorf.

Rheo-VSANS measurements were performed to characterize the interactions within silica colloidal particles in concentrated dispersions to extract the science behind the particle interactions and enhance the capacity of colloidal particle processing, including sustainable mineral beneficiation of complex ores. For colloidal particle processing, its proper dispersion/liberation plays a key role in achieving a good performance in processing plants (e.g., selective enrichment of valuable minerals from natural ores). Hence, precise characterization and manipulation of particle dispersion and coagulation in processing media are necessary. Currently available methods for colloidal particle characterization (e.g., turbidity, zeta potential) often require a dilute suspension. Thus, they could overlook the coagulation potentially occurring in highly concentrated suspensions which are commonly treated in plant operations. This coagulation can be caused by an increase in the particle–particle interactions as suspension concentration increases. This proposed work is to develop a Rheo-VSANS method for studying the changes in particle spacing and structure in concentrated suspensions/dispersions and discuss the abovementioned point.

4.1.2 Materials and methods

Micronsize silica particles dispersed in glycerol–water mixture (with different mass ratio = 90:10, 75:25, 50:50) at 40 vol.% and different solution pH (2, 6, 10) were measured with MCR301 (Anton Par) and a cone geometry (diameter = 49.962 mm, angle = 0.999, truncation = 100 μm , CP50-1/S, Anton Paar) and a rough metal plate to avoid slipping as a function of shear rate (1/s) from 0.005 to 500, and 500 to 0.005 with the five points per decade data acquisition. Repeat three cycles of upward and downward measurements and examine the reproducibility of second and third cycles. When uncertainty was observed, further measurement cycle(s) was performed.

Rheo-SANS measurements were conducted in the q range from 4×10^{-5} to $2 \times 10^{-3} \text{ \AA}^{-1}$ at a VSANS beamline for dispersions made of the same silica particles. Materials were first mixed in an electrolyte solution of potassium nitrate ($1 \times 10^{-2} \text{ M}$) made of the mixture of D_2O and Milli-Q water in different ratio as a medium to minimize the effects of multiple scattering (Otsuki et al., 2018). Solid concentrations were adjusted to between 1 and 40 vol.% based on our previous study. Once a dispersion was evenly mixed, its pH was adjusted using HNO_3 or KOH followed by conditioning for 30 min. The dispersion was then transferred into a cylindrical cell for rheo-SANS. Measurements were performed two single particles (i.e., SiO_2) different pHs (2, 6, 10) for changing the particle interactions at three to five different shear rates (i.e., $1\text{--}500 \text{ s}^{-1}$) to study the effect of shear rate on the correlation between microscopic particle interactions and macroscopic rheological behavior of particles/aggregates as well as correlation peaks and I-Q slope to investigate the changes in interparticle distance and structure of particles/aggregates, respectively.

4.1.3 Results and discussion

Suspension rheology at a laboratory confirmed the typical shear thickening behavior with our polydisperse silica colloidal particle suspensions. The flow curve shown in Fig. 11.7 indicates the decrease of suspension viscosity till a certain shear rate of approximately 5 s^{-1} and then increased again above that threshold shear rate. This agreed with many of the literature reporting the shear thickening behavior with monodisperse silica particle suspensions (e.g., Mewis and Wagner, 2012).

Rheo-VSANS measurements were performed with concentrated silica particle suspension that was reported as a shear thickening fluid behaving like a solid upon significantly high enough load (critical shear rate) applied to the suspension (e.g., Mewis and Wagner, 2012; Fall et al., 2012). In our study, no apparent scattering anisotropy was observed above the critical shear rate (Fig. 11.8) against our expectation based on previous reports on monodisperse silica particle suspensions while the hydrocluster formation in that shear rate from the rheological measurements above the critical shear rate was observed (Fig. 11.7). Here, the author would like to point out that our previous investigation with USANS 1D detector system also did not allow capturing this anisotropy. This can be explained by the polydispersity of the particles in terms of the size and shape that can be the cause of minimizing the anisotropy in the scattering patterns of suspensions composed of those particles (Otsuki et al., 2018; Otsuki, 2019). It would be interesting to investigate and further understand the effects of degree of polydispersity on the anisotropy with model particle systems (Fig11.8).

On the other hand, scattering curves obtained at different shear rates indicated some difference. Fig. 11.9 shows that the scattering intensity at the lowest q increases with shear rate, indicating the hydrocluster formation enhanced with higher shear load application (from 25 to 500 s^{-1}). In other words, the population of large particles increased with shear rate, indicating the presence of hydrocluster

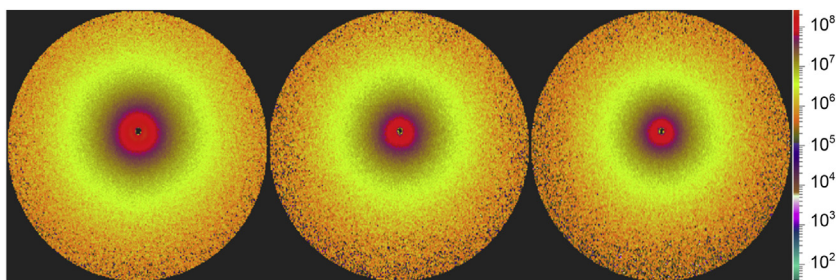


FIGURE 11.8

2D scattering patterns obtained with silica particle suspension prepared at 40 vol.% at pH 10 and measured at different shear rate of 500, 50, and 25 s^{-1} .

From right to left Otsuki, A., June 2019. Rheo-SAS: feasibility to characterize concentrated colloidal particle suspensions for their processing. Proc. European Metallurgical Conference 2019, Dusseldorf.

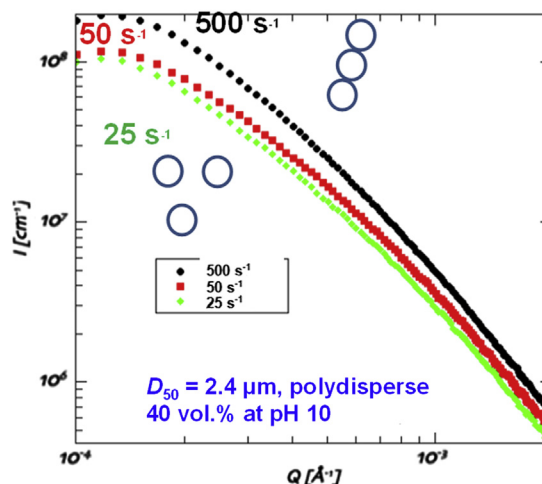


FIGURE 11.9

Scattering intensities of silica particle suspension prepared at 40 vol.% at pH 10 and measured as a function of different shear rates.

Modified from Otsuki, A., June 2019. Rheo-SAS: feasibility to characterize concentrated colloidal particle suspensions for their processing. Proc. European Metallurgical Conference 2019, Dusseldorf.

formation correlated with the global rheology curve presented in Fig. 11.7 showing the viscosity increase above 5 s^{-1} till 500 s^{-1} . Other than that point, the two scattering curves at 25 and 50 s^{-1} fall into the similar line with the slope of q^{-2} to q^{-3} , while the slope of the curve obtained at 500 s^{-1} is closer to q^{-3} . It implies the particle shape is spherical and there are some changes in surface structure, e.g., aggregation of fine particles on the surface of larger particles.

5. Summary and future perspectives

In this article, the issues associated with colloid dispersions/suspensions were first discussed in relation to the formulation with increasing their concentration that is a general trend in many of colloidal processing industries. The scattering theory was then introduced to evaluate the microscopic particle–particle interaction in colloidal systems and their stabilities in coupling with rheological measurement for macroscopic suspension behavior. This article also reports our attempts of developments and investigations on in situ rheological measurements with very small-angle scattering (rheo-VSAS) measurements of suspensions composed of polydisperse colloidal particle suspensions. Laboratory rheological measurements in a cone-plate geometry confirmed that the shear thickening behavior of colloidal silica particle suspensions despite their polydispersity agreed with previous reports

measuring monodisperse particle suspensions. Our suspensions were also measured in a rheo-VSANS setup and acquired scattering curves under different shear rates with different suspension formulations. The in situ measurement in the neutron facility also exhibits the shear thickening behavior in a bob and cup geometry, while the anisotropy in the 2D scattering patterns were not clearly identifiable probably due to the polydispersity in the system. On the other hand, scattering curves obtained at different shear rates indicated some difference. Thus, further tuning the systems and setup is highly recommended to extract some useful results from this unique coupling of rheology and scattering in case of its application to complex systems (e.g., polydisperse systems, heterocoagulation systems (Otsuki et al., 2011)).

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Dynamic rheology and mechanics of polymers in their solid state

12

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Abstract

This chapter presents an overview of the dynamic rheological and mechanical properties of polymers in their solid state. Under large deformation, the material response of polymers is no longer linear viscoelastic, and different techniques have been proposed to analyze the nonlinear behavior of these materials. The current techniques and theories are presented, but Fourier transform (FT) rheology is more detailed.

Furthermore, this chapter deals with the mechanical fatigue of polymers. The basic concepts are presented first using the well-known Wöhler curves representation of the number of cycles to failure as a function of the applied stress (stress controlled) or strain (strain controlled) amplitude. Secondly, a discussion is made on the different approaches to follow the material properties' changes during testing/application such as the dissipated energy function, the nonlinear viscoelastic parameter, and the analysis of higher harmonics of the stress response via FT. Finally, the current investigation trends are presented.

Keywords: Dynamic rheology; Fourier transform rheology; Mechanical fatigue; Nonlinearity.

1. Introduction

The world plastic production rapidly increased since the 1950s from 1.5 to more than 300 Mt/y today (2018). About one-third of the world plastic production is used for packaging, another third in buildings (pavements, windows, and piping), while the last third includes industrial components (automotives, toys, and furniture) (Andrady and Neal, 2009). In several applications, plastic parts replaced common materials (metals, woods, and ceramics) because they provide various advantages such as a low density, corrosion resistance, a wide range of processing possibilities to allow basically all shapes of the final part in combination with low costs, especially for the so-called commodity plastics like polyethylene and polypropylene.

But polymers are viscoelastic materials and show, in the melt and solid state, a nonlinear response when the deformation exceeds a certain threshold.

Viscoelasticity implies that the stress response contains both an elastic and a viscous part characterized by the storage E' and loss E'' moduli in tension, or G' and G'' in shear/torsion. Nonlinearity means that the stress response is no longer proportional to the load/deformation. Under simple shear, the viscosity might decrease/increase as a function of the applied shear rate after a constant plateau value at small deformations/rates (Bird et al., 1987; Carreau et al., 1997). Under oscillatory shear, the stress response becomes nonlinear, so the parameters G , E , η , etc., are no longer constant, but depend on the applied conditions. During oscillatory shear, higher harmonics (through FT) can be detected (Giacomin and Dealy, 1993; Wilhelm, 2002).

The rheological properties of melts are of high importance for polymer processing. Therefore, it is important to know the viscosity at a given temperature and shear rate, as well as how it is influenced by their changes in processes like extrusion, injection molding, etc.

One of the main limitations with respect to the application of every solid part is its lifetime. In particular, the failure of a solid material under a repetitive load is called mechanical fatigue (Andrew, 1995), which is responsible for about 90% of all the mechanical service failures (Campbell, 2008). For our daily life, safe use without the fear of failure is of fundamental interest.

It is a challenge to predict the long-term performance of a material under a load. The first publications on the systematic analysis of fatigue can be found from the 1830s by English, French, and German engineers, investigating the then-new phenomenon of cyclic fatigue of metal in construction and machines like railways. The most well-known name related to fatigue at that time is August Wöhler (“Versuche über die Festigkeit der Eisenbahnwagenachsen” (“Study on the Stability of Railroad Vehicle Axes”)) (Wöhler, 1867)), who analyzed the (sinusoidal) number of cycles (N) to failure of a metal dumbbell sample as a function of the applied stress amplitude (S), nowadays known as Wöhler or S – N curve. However, Wöhler curve is an old characterization tool for mechanical fatigue under dynamic loading, but is still state-of-the-art as it represents the simplest way to characterize and quantify the fatigue resistance of a material. The main drawback of Wöhler curves are their typically large standard deviations (Bathias and Pineau, 2013), and the resulting limited meaning for an individual sample. The deformation mode of choice is nowadays sinusoidal and can be performed with a low signal to noise (S/N) ratio.

The mechanical fatigue testing of polymers must also take a polymer-specific property into account: their viscoelasticity and their nonlinearity at large strain amplitudes (Sauer and Richardson, 1980). Recent methods of fatigue analysis in deformation/strain controlled tests, providing more information about the current state of fatigue, without using additional devices (camera), are based on the stress response analysis of the material. The stress response can be analyzed in strain/strain rate or time domains. In the strain domain (hysteresis loops or so-called Lissajous curves), although (large) changes can be seen by the naked eye, they can hardly be quantified. In the time domain, different parameters and analysis methods exist based on an FT of the stress. As an example, the nonlinear viscoelastic parameter

(NVP) was proposed which represents the sum of the stress higher harmonics over the fundamental one, analog to the total harmonic distortion for sound systems. Another approach is to analyze the higher harmonics separately which has the advantage, especially in torsion/shear, of separating between the material-dependent parameters (higher odd harmonics) and parameters related to asymmetry in the stress response (higher even harmonics). These concepts are described next.

2. Viscoelasticity of solid polymers

2.1 Viscoelasticity of polymers

Rheology investigates the flow behavior of materials under deformation. The basic parameters are therefore the normalized deformation, the strain (γ), and the resistance force (F) of the material, typically normalized by the loaded surface (A) to get a system-independent quantity, which is the stress (σ):

$$\sigma = \frac{F}{A} \quad (12.1)$$

Static and dynamic deformations can be applied to a material, but the focus here is on dynamic (sinusoidal) deformations.

2.1.1 Linear viscoelasticity

The typical models to describe elasticity and viscosity are the ideal elastic solid and the ideal viscous fluid, represented by a spring and dashpot (mechanical analogy). The ideal elastic solid can be described by Hooke's law with the modulus G as the proportional constant between strain and stress. Newton's law describes the stress for an ideal viscous fluid, with the viscosity η as the proportional factor between shear rate and stress.

$$\sigma = G\gamma \quad (12.2)$$

$$\sigma = \eta\dot{\gamma} \quad (12.3)$$

Models to describe the rheological and mechanical behavior of viscoelastic materials combine typically spring and dashpot (Hooke's and Newton's law), respectively, in different numbers and ways. The simplest viscoelastic solid model is the Kelvin–Voigt model, combining spring and dashpot in parallel. On the other hand, the Maxwell model combines spring and dashpot in series for a viscoelastic liquid. More advanced models are also available (Burgers, Jeffreys, etc.).

Under small amplitude oscillatory shear (SAOS), the stress response is linear with the strain amplitude, i.e., if the strain is sinusoidal, the stress is sinusoidal as well, but with a lag. A complex notation can be used, so the strain is written as follows (according to Euler's rule):

$$\gamma = \gamma_0 e^{i\omega_1 t} \quad (12.4)$$

$$\sigma = I_1 e^{i\omega_1 t + \delta_1} \quad (12.5)$$

Consequently, the stress response under oscillatory shear can be completely mathematically described by a complex function with the magnitude I_I and phase angle δ_I . The magnitude I_I divided by the strain amplitude is the complex modulus (G^*) and, together with the phase angle, forms a set to describe in a complex plane the real (G') and imaginary part (G''). This regime is called the linear or SAOS regime. In the linear regime, the storage and loss moduli are independent of the applied strain amplitude and provide rheological parameters to completely characterize a material in a meaningful way.

2.1.2 Nonlinear viscoelasticity

In the nonlinear regime, under the conditions of large amplitude oscillatory shear (LAOS), the above statements do not hold anymore. Consequently, G' and G'' depend on the applied strain amplitude. Fig. 12.1 presents an example for G' and G'' as a function of the strain amplitude. For small strain amplitudes, G' and G'' are constant and independent of the strain amplitude, but they can increase/decrease for larger strain amplitudes, so

$$G = G(\gamma_0) \neq \text{constant} \quad (12.6)$$

For fluids, four main types of G' and G'' behavior as a function of strain amplitude were described (Hyun et al., 2002). When G' and G'' decrease with increasing strain, strain softening (Type I) occurs, while the reverse is called strain hardening (Type II). If G' decreases but G'' increases before decreasing, leading to a weak strain overshoot (“Payne effect” for filled rubbers), this is associated to Type III. Finally, when both parameters increase before they decrease with a strong strain overshoot, Type IV is obtained. However, mixed behaviors out of these four main types have been reported.

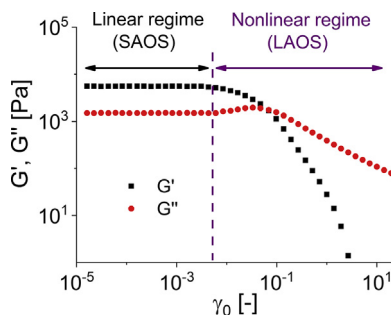


FIGURE 12.1

Typical G' and G'' behavior during a strain sweep test in the linear (SOAS) and nonlinear (LAOS) regime of a polylactic acid/nanocrystal composite (PLA2002D, $M_n = 12.5$ kg/mol) at $\omega/2\pi = 1$ Hz and $T = 165^\circ\text{C}$.

According to Hyun K., Kim S.H., Ahn K.H., Lee S. J., 2002. Large amplitude oscillatory shear as a way to classify the complex fluids, *J. Non Newtonian Fluid Mech.* 107, 51–65, <https://doi.org/10.1007/s13367-011-0028-0>.

A stress versus strain curve (so-called Lissajous curve) can be plotted for each cycle. The shape of a Lissajous curve is a straight line for an ideal elastic body and a circle for an ideal viscous one (Larson and Dealy, 2006). Consequently, the shape of the Lissajous curve can be correlated to the material viscoelasticity. It shows if a viscous or elastic behavior dominates and if the stress response is linear or not. However, Lissajous curves can hardly detect small nonlinear contributions and are unable to quantify them.

2.2 Large amplitude oscillatory shear

2.2.1 Fourier transform

The FT is a reversible mathematical function decomposing a signal into a sum of sine and cosine functions or (using Euler's approach) a sum of exponentials (Brigham, 1974). It calculates the periodic contributions of a time signal, displaying their amplitudes and phases (or in a complex plane as the real and imaginary parts) as a function of frequency.

The FT of any real or complex time signal $s(t)$, or frequency-dependent spectrum $S(\omega)$ (inverse FT), is typically defined as follows:

$$S(\omega) = \int_{-\infty}^{\infty} s(t) e^{-i\omega t} dt \quad (12.7)$$

$$s(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(\omega) e^{i\omega t} d\omega \quad (12.8)$$

Moreover, the FT is an orthogonal (linear) transform. Consequently, the sum of two functions in the time domain corresponds to their sum in the frequency domain (Bracewell, 1986).

$$as(t) + bg(t) \leftrightarrow aS(\omega) + bG(\omega) \quad (12.9)$$

Because the FT transposes a real (time) signal into a complex (frequency) signal, an FT spectrum contains real and imaginary parts. In the complex plane, each signal can be considered as a vector from the origin with a magnitude I_ω and a phase $\varphi(\omega)$.

2.2.2 Fourier transform rheology

The stress response becomes nonlinear under LAOS conditions (Giacomin and Dealy, 1993). Nonlinearity means in this context that the stress and strain rates are not directly proportional to each other.

$$\sigma \neq \gamma, \dot{\gamma} \quad (12.10)$$

From an experimental point of view, this means that the modulus and viscosity are affected by the testing conditions (strain/strain rate, see Fig. 12.1). The linear parameters G' and G'' are sufficient to describe the stress response completely in the linear case (Eqs. 12.2 and 12.3). However, this is not enough in the nonlinear regime so they partially lose their (physical) meaning. Therefore, it is necessary to use a more advanced approach to completely describe the stress response.

Currently, the nonlinear stress response was analyzed quantitatively in the strain/strain rate (Cho et al., 2005; Ewoldt et al., 2008) or the time domain (Hyun et al., 2011; Wilhelm, 2002). In the strain/strain rate domain, the corresponding Lissajous curves are decomposed into elastic and viscous moduli, by using Chebyshev polynomials, for example. In the time domain, the stress signal is decomposed into a Taylor series of odd higher harmonics of the deformation frequency, using FT. This decomposition is better done in the time domain because it is easier to analyze for a time-dependent process like fatigue. However, Fourier series can be converted into Chebyshev coefficients and vice-versa.

2.2.2.1 Odd higher harmonics

The FT of the nonlinear stress response only shows odd higher harmonics, as shown in a typical FT spectrum presented in Fig. 12.2.

This can be explained using the simplest nonlinear 1D scalar model for an elastic solid body, a nonlinear spring (Doetsch et al., 2003). In such a model, the spring constant (which corresponds to the modulus) depends on the strain:

$$\sigma = G(\gamma)\gamma \quad (12.11)$$

Additionally, it is assumed that the modulus of the clockwise half cycle $G^*(\gamma^+)$ is equal to the counterclockwise cycle $G^*(\gamma^-)$, which is a reasonable assumption for isotropic materials. As a result, the (complex) modulus depends only on the absolute values of the strain:

$$G(\gamma^+) = -G(\gamma^-) = G(|\gamma|) \quad (12.12)$$

$$\sigma = G(|\gamma|)\gamma \quad (12.13)$$

Consequently, if the absolute value of the modulus is expanded in a Taylor series of the strain, only even powers are obtained:

$$G(|\gamma|) = G_1 + a_1\gamma^2 + b_1\gamma^4 + \dots \quad (12.14)$$

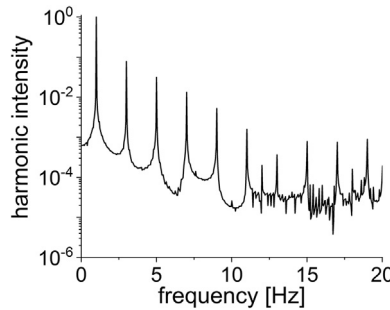


FIGURE 12.2

Fourier spectrum of the stress response of a polylactic acid/nanocrystal composite (PLA2002D, $M_n = 12.5$ kg/mol) at $\gamma_0 = 268\%$, $\omega/2\pi = 1$ Hz, and $T = 165^\circ\text{C}$. The signal to noise (S/N) ratio is in the range of 100,000:1.

Inserting Eqs. (12.4) and (12.14) in Eq. (12.13) gives

$$\sigma = G(|\gamma|)\gamma = (G_1 + a_1\gamma^2 + b_1\gamma^4 + \dots)\gamma_0 e^{i\omega_1 t} \quad (12.15)$$

$$\sigma = G_1\gamma_0 e^{i\omega_1 t} + a_1\gamma_0^3 e^{3i\omega_1 t} + b_1\gamma_0^5 e^{5i\omega_1 t} + \dots \quad (12.16)$$

which can be rewritten as follows:

$$\sigma = I_1 e^{i\omega_1 t} + I_3 e^{3i\omega_1 t} + I_5 e^{5i\omega_1 t} + \dots \quad (12.17)$$

To better quantify and compare a nonlinear behavior, mostly the third harmonic ($I_{3\omega_1}$) is considered and normalized to the fundamental harmonic (I_{ω_1}) typically written as ($I_{3/I}$). From Eqs. (12.16) and (12.17), it can be seen that the n th harmonic depends on the n power of the strain amplitude and consequently the $I_{n/I}$ intensity depends on $(\gamma_0)^{n-1}$. The $I_{3/I}$ intensity in a strain sweep test, including linear and nonlinear regime, typically follows the behavior described in Fig. 12.3 (log-log plot).

Firstly, the $I_{3/I}$ intensity decreases with a slope of -1 , before it increases with a slope of 2 and levels off to a constant value at very large strain amplitudes. The decrease of $I_{3/I}$ with a slope of -1 (mostly in the SAOS regime) is caused by the sensitivity limit of the torque transducer (Eq. 12.18) (Reinheimer et al., 2012). Below the minimum instrument torque resolution, I_n cannot be detected and can be assumed to be equal to noise N :

$$I_n \sim \frac{N}{I_1} \sim \frac{N}{\gamma_0} \sim \gamma_0^{-1} \quad (12.18)$$

The increasing part of the curve with a slope of 2 is also theoretically expected (Eq. 12.17). However, theoretical calculations predict that $I_{3/I}$ quadratically depends on the strain amplitude even in SAOS, but its values become negligibly small ($<10^{-4}$ – 10^{-5}) (Merger et al., 2016). Therefore, it is important to mention from an experimental point of view that for a given (nonlinear) viscoelastic material,

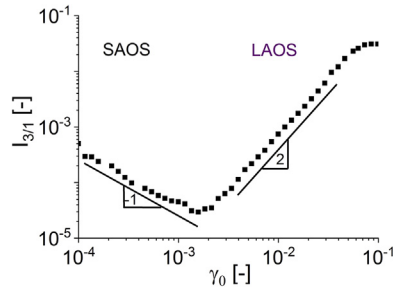


FIGURE 12.3

Typical response for the third harmonic ($I_{3/I}$) intensity as a function of the applied strain amplitude (γ_0), showing the behavior in SAOS and LAOS of a polylactic acid/(treated) nanocrystal composite (PLA2002D, $M_n = 12.5$ kg/mol) at $\omega/2\pi = 1$ Hz and $T = 165^\circ\text{C}$.

the strain amplitude of the $I_{3/1}(\gamma_0)$ minimum does not represent the transition between SAOS and LAOS. It is an instrument-related property as it depends on the signal to noise ratio (resolution) of the torque transducer, the oversampling, the sampling rate, etc.

2.2.2.2 The intrinsic nonlinearity Q_0

The nonlinear parameter $I_{3/1}$ (and higher odd harmonics) quantifies the level of material nonlinearity at a given strain amplitude. For a general material nonlinearity quantification, a measurement condition independent quantity must be used. After the minimum, the $I_{3/1}$ intensity scales quadratically with γ_0 before leveling off, following a power-law relation (Cziep et al., 2016; Hyun and Wilhelm, 2009):

$$Q = \frac{I_3}{\gamma_0^2} \quad (12.19)$$

For each material (and temperature/frequency), Q is constant over a range of strain amplitudes and a parameter can be defined characterizing the material which is independent of the applied strain amplitude:

$$Q_0 = \lim_{\gamma_0 \rightarrow 0} Q = \frac{I_3}{\gamma_0^2} \quad (12.20)$$

2.2.2.3 Even higher harmonics

As described in Section 1 for isotropic materials ($G(\gamma^+) = G(\gamma^-)$), only odd higher harmonics should be obtained in the stress FT spectrum under LAOS conditions. However, higher even harmonics, typically with a lower intensity than the odd ones ($I_{2/1} < I_{3/1}$, $I_{4/1} < I_{5/1}$, etc.), can be observed. For isotropic materials, these even higher harmonics are mostly related to measurement artifacts on the macroscopic level, besides the error range of the experiment (lack of sensitivity), for example, wall slip (Hatzikiriakos and Dealy, 1991) or inertia (Atalık and Keunings, 2004). However, Sagis et al. (2001) theoretically predicted and experimentally showed the occurrence of even harmonics in the stress response caused by changes on a microscopic level. For demonstration purpose, they used a viscoelastic material with anisotropic rigid particles. Their main statement is that for broken shear symmetry to occur ($G(\gamma^+) \neq G(\gamma^-)$), odd and even harmonics are needed to completely describe the stress response. Moreover, Sagis et al. (2001) were able to theoretically and experimentally show that higher even harmonics first increase with increasing deformation, go to a maximum, and then decrease at very large strain amplitudes.

3. Mechanical fatigue

This section describes the most important approaches related to the methodology and analysis of dynamic fatigue testing. The experiments can be performed under controlled (constant) strain or stress. The main focus here is on a strain controlled

approach, as it is the most used toward continuous signal analysis. In strain controlled fatigue testing, the strain amplitude is constant, typically following a sine function. The stress response as a function of the number of cycles can be presented by hysteresis loops/Lissajous curves as described in Fig. 12.4. Furthermore, the strain amplitude, as well as the experimental setup/conditions (sampling rate), must be carefully chosen to completely analyze the stress signal higher harmonics during a fatigue test.

3.1 Different loading modes

Fatigue tests can be performed under different loading conditions like shear or torsion, tension/tension, tension/compression, three-point bending/dual cantilever, etc. An important characteristic for the test results comparability and the higher harmonics contribution prediction is the stress ratio (R), which is defined as ratio between the minimum and maximum stress:

$$R = \frac{\text{minimum stress}}{\text{maximum stress}} \quad (12.21)$$

Under oscillatory shear and three-point bending/dual cantilever geometries, the stress ratio (R) is usually equal to -1 , as it is not necessary to use a preload. This simplifies the higher harmonics analysis and interpretation because the same higher harmonics are expected as in the rheology of polymer melts under LAOS conditions. Consequently, only odd higher harmonics are expected, representing

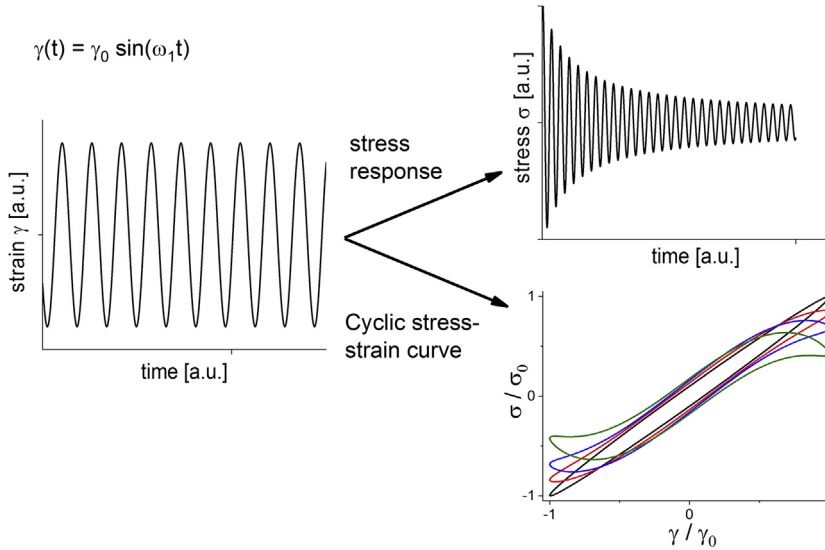


FIGURE 12.4

Typical behavior of the stress response of a strain controlled fatigue test and its corresponding hysteresis loops/Lissajous curves.

the material viscoelastic nonlinearity. In cases when the even harmonics intensity increases above the noise level during a test, this indicates that the stress signal is not symmetric anymore and could be related to the appearance of macroscopic cracks (Hirschberg et al., 2017).

However, a preload results in higher even harmonics above the noise level making the higher harmonics interpretation more complex. But in tension/tension, the deformation oscillates around a preload value, larger than the deformation amplitude to avoid compression. At large oscillatory strain amplitudes and consequently large preloads, the stress response during the half cycle to the stress maximum is different than the one back to the stress minimum. Consequently, the stress signal is not symmetric and contains even and odd higher harmonics. This makes more difficult the interpretation of these higher harmonics because it is not clear which harmonics are caused by the material nonlinearity compared with the stress signal asymmetry due to the loading conditions. The same comment is also valid for tension/compression, compression/compression, and three-point bending tests.

3.2 Wöhler curves

The first systematic approach for testing and analyzing dynamic mechanical fatigue data can be traced back to the 19th century with the work of August Wöhler (Wöhler, 1867). Wöhler studied the dynamic mechanical fatigue of metal specimen under a constant load (stress controlled). The number of cycles to failure was analyzed as a function of the applied load/stress, resulting in stress-number of cycles to failure ($S-N$) or in so-called Wöhler curves. Wöhler curves have typically three different regimes (Fig. 12.5).

Firstly, the low cycle fatigue regime is associated to high stress amplitudes. In this case, the stress amplitude is very high and the samples fail within a few cycles

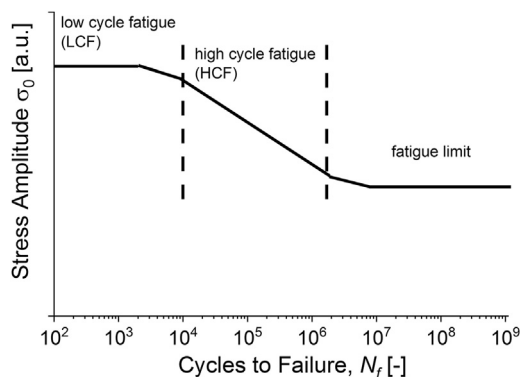


FIGURE 12.5

Schematic representation of a Wöhler curve with the three typical regimes: low and high cycle fatigue, followed by the fatigue limit.

(N_f), typically less than 10^3 – 10^4 . Secondly, for lifetime between 10^4 and 10^6 cycles, N_f depends on the stress amplitude via a power law. Finally, if the stress is not sufficient to break the sample, the fatigue limit is reached. However, the stress amplitude on real samples still has an effect in this regime, resulting in a substantial lifetime improvement with decreasing stress amplitude. The same approach can be used for strain controlled tests, resulting in strain-number of cycles to failure curves. In the high cycle fatigue regime, the number of cycles to failure is typically a function of the strain amplitude via a power law as follows:

$$N_f = B\gamma_0^C \quad (12.22)$$

3.3 Approaches following the material properties

Generally, the number of cycles to failure varies over a wide range under a given loading condition, i.e., up to four orders of magnitude have been reported (Campbell, 2008). Therefore, Wöhler curves are a statistical approach to predict the most probable number of cycles to failure (Sivak and Ostertagová, 2012), and their predictive power for a single sample or application is very limited as a more precise prediction is in general not possible. Consequently, more in-depth understanding of the fatigue state during an ongoing process is needed to better predict and understand failure. As a result, several approaches have been developed, following the material's properties as a function of time or cycle number. Most of these approaches are based on two polymer-specific properties: their viscoelasticity and their nonlinearity at large strain amplitudes. On the one hand, the loss modulus of polymers is high compared to metals due to their highly viscoelastic behavior resulting in high energy dissipation during each cycle of the fatigue process. On the other hand, the nonlinear stress response at large strain amplitudes can be followed. Mechanical fatigue is known to produce increased nonlinearity in the material's stress response, thus the shape of the Lissajous curve is changing to become more nonlinear (Lacroix, 2004; Liang et al., 1996; Mortazavian and Fatemi, 2015).

3.3.1 Concepts related to the dissipated energy

Polymers are viscoelastic materials, so energy is dissipated as heat under loading. In comparison to metals, this polymer-specific property must be taken into account for the analysis and understanding of fatigue results. The dissipated energy (DE) for polymers is high in comparison to metals due to a much higher $\tan(\delta_1)$ value of about 10^{-1} (Ward and Sweeney, 2004), in comparison to 10^{-5} for metals.

3.3.1.1 Viscous heating

The area enclosed by a Lissajous curve represents the DE during a cycle. For ongoing fatigue in strain controlled tests, it was observed that the slope of Lissajous curves decreases and their area increases (Wang et al., 1984). Consequently, the

amount of DE increases during the test, before decreasing due to sample failure. For a sinusoidal deformation, the following equation can be obtained (Ganeriwala and Rotz, 1987):

$$DE = \int_{-\gamma}^{\gamma} \sigma d\gamma = \pi \gamma_0^2 G'' \quad (12.23)$$

According to literature (Ewoldt et al., 2010; Ganeriwala and Rotz, 1987), this relation is still valid in the nonlinear regime, so that G'' is a simple way to analyze the DE during a fatigue test and consequently no nonlinear changes must be considered.

The heat dissipation can result, especially in stress controlled tests, in a substantial sample temperature increase, initially slow before increasing due to the so-called thermal runaway. An increasing temperature is self-evident due to viscous heating, but thermal runaway is a result of mechanical fatigue and a temperature dependency of the polymers moduli. At first the mechanical fatigue softens the specimen and to keep the stress amplitude constant, the strain amplitude increases. This results in an increase of dissipated heat. Consequently, the moduli further drop, leading to an increasing strain amplitude and resulting in more heat dissipated. This process continues until the specimen melts or is destroyed by too large strain amplitudes (Crawford and Benham, 1974). A strain controlled test does not show this behavior because the stress amplitude to achieve the set strain amplitude only decreases. Thus, in comparison to stress controlled experiments, less energy is dissipated and thermal runaway can be prevented.

The first research related to DE during fatigue testing was done in the 1920s on metal specimens (Inglis, 1927). Since then, several approaches for (viscoelastic) materials have been introduced, for example, the correlation between the DE during the complete test (cumulative DE) or the so-called ratio of dissipated energy change (RDEC) with the lifetime.

The first approaches correlating the cumulative DE and the number of cycles to failure in a power-law relation, as described in Eq. (12.24), were specified by Halford et al. for metals in 1966 and by Van Dijk and Visser et al. in 1977 for viscoelastic materials like bitumen.

$$W_f = A_W N_f^\alpha \quad (12.24)$$

Moreover, Hopman et al. (1989) introduced the so-called RDEC, dividing the difference of DE between two consecutive cycles to the first one as follows (Hopman et al., 1989; Pronk and Hopman, 1991):

$$RDEC = \frac{DE_{n+1} - DE_n}{DE_n} \quad (12.25)$$

Three regimes were found in the (time-dependent) RDEC evolution for strain controlled tests of viscoelastic materials like bitumen mixtures (Pronk and Hopman, 1991). In regime I, RDEC rapidly decreases and levels off to a plateau value (PV)

in regime II, before substantially increasing in regime III due to failure onset. The PV was correlated to the number of cycles for a 50% decrease in stiffness and a power-law correlation was proposed by [Shen and Carpenter \(2005\)](#).

3.3.2 Concepts related to nonlinear changes in the stress response

3.3.2.1 Viscoelastic nonlinear parameter

As described above, polymers are viscoelastic materials and their stress response is nonlinear beyond a critical strain, which increases with ongoing fatigue. Consequently, it makes sense to quantify nonlinear changes in the stress response to correlate with fatigue. The *NVP* was proposed to quantify the nonlinear behavior by calculating the ratio between the sum of higher harmonics (I_n) via FT of the stress over the fundamental one (I_1) as follows:

$$NVP = \frac{I_2 + I_3 + I_4 + \dots + I_n}{I_1} \quad (12.26)$$

with n usually between 10 and 100 ([Liang et al., 1996](#); [Noda et al., 2001](#); [Komatsu et al., 2003](#)). During a fatigue test ([Fig. 12.6](#)), the *NVP* typically increases and reaches its maximum shortly before being broken. This method was applied for tests with different loading modes tension/tension, tension/compression, and compression/compression ([Komatsu et al., 2003](#); [Liang et al., 1996](#); [Noda et al., 2001](#)). However, this parameter has several drawbacks as it depends on the parameter n (arbitrary) and test setup conditions (sampling rate, signal to noise ratio, etc.). The final value also sums up a lot of noise. This not only results in limited reproducibility (see [Fig. 12.6](#) before the *NVP* increases rapidly) but also impedes the detection of small changes in higher odd harmonics and consequently reduces its meaning.

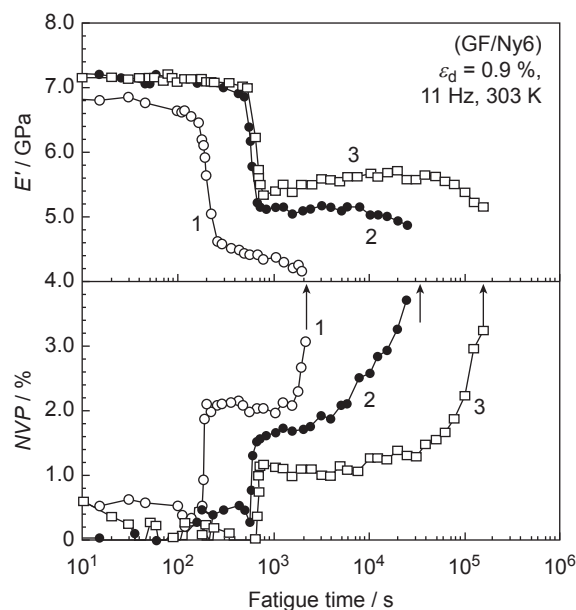
Furthermore, higher odd and even harmonics are not analyzed separately, neglecting a large amount of information coming from the different higher harmonics. Another drawback of the test setup, which will be discussed more in detail in the next section, is the exact meaning of higher harmonics when $R \neq -1$.

3.3.2.2 Analysis of higher harmonics in the stress response

Separately analyzing odd and even higher harmonics was first introduced by Lacroix in 2004 on rubber materials. More recently, [Hirschberg et al. \(2017\)](#) used this method on thermoplastics. The advantage of separately analyzing odd and even higher harmonics is that (physical) meaningful parameters (odd ones) are separated from those caused by noise, measurement artifacts, and symmetry arguments (even ones).

3.3.2.2.1 Thermoplastics. [Hirschberg et al. \(2017\)](#) performed (strain controlled) fatigue tests using rectangular polystyrene samples, in the material's viscoelastic nonlinear regime and calculated the higher harmonics in the stress response via FT.

The intensities of the higher harmonics (normalized to the fundamental one) were separately analyzed, in particular the first odd higher harmonic ($I_{3/1}$) and the

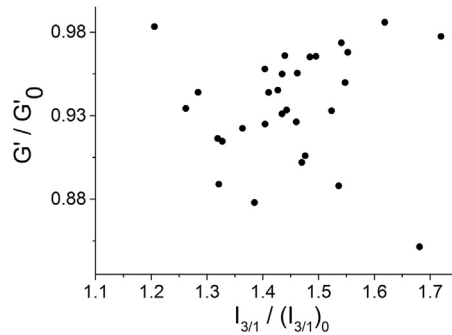
**FIGURE 12.6**

Storage modulus (E') and nonlinear viscoelastic parameter as a function of time for three different loading modes of a glass fiber/Nylon6 (GF/Ny6) sample: tension/tension (empty circle), tension/compression (full circle), and compression/compression (empty square) at $\omega/2\pi = 11$ Hz and $T = 303$ K.

Komatsu S., Takahara A., Kajiyama T., 2003. Effect of cyclic fatigue conditions on nonlinear dynamic viscoelasticity and fatigue behaviors for short glass-fiber reinforced Nylon6, *Polym. J.* 35, 844–850. <https://doi.org/10.1295/polymj.35.844>.

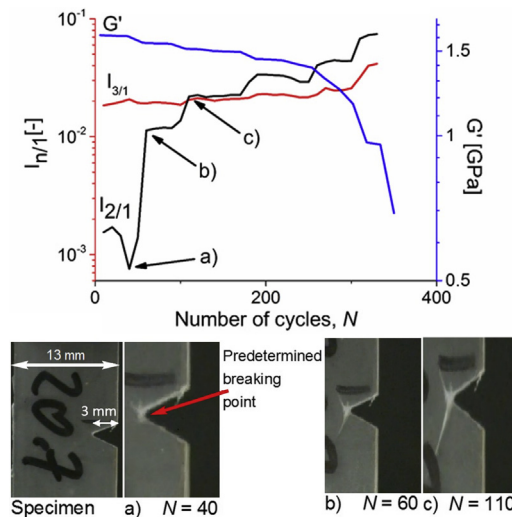
first even higher harmonic ($I_{2/1}$). Further higher harmonics were found to be close to the noise level and to behave similarly to the first even/odd ones. The evolution of the material properties was followed by analyzing the storage modulus and the first odd harmonic ($I_{3/1}$). Changes up to the crack occurrence were analyzed and $I_{3/1}$ was found to be a more sensitive threshold than G' . Until the initiation of a macroscopic crack, G' typically decreases by $7.5 \pm 5\%$, while the $I_{3/1}$ intensity typically increases by $45 \pm 10\%$ (Fig. 12.7).

The first even harmonic ($I_{2/1}$) was found to be a highly sensitive parameter to the occurrence of macroscopic cracks. When macroscopic cracks occur, the $I_{2/1}$ intensity was found to drastically increase as described in Fig. 12.8. In this case, the occurrence of a macroscopic crack (between $N = 40$ and $N = 60$ cycles) results in an increase of $I_{2/1}$ intensity from below 10^{-3} by over a factor of 10 to above 10^{-2} . Values up to 800% have been observed. This could be explained by the broken

**FIGURE 12.7**

The (normalized) decrease of G' against the (normalized) increase in $I_{3/1}$ until a macroscopic crack occurred in polystyrene.

Hirschberg V., Wilhelm M., Rodrigue D., 2017. Fatigue behavior of polystyrene (PS) analyzed from the fourier transform (FT) of stress response: first evidence of $I_{2/1}(N)$ and $I_{3/1}(N)$ as new fingerprints, *Polym. Test.* 60, 343–350. <https://doi.org/10.1016/j.polymertesting.2017.04.001>.

**FIGURE 12.8**

Storage modulus (G') and $I_{2/1}$ and $I_{3/1}$ intensity as a function of the number of cycles (N). The $I_{2/1}$ intensity increases substantially (over a factor of 10) when a macroscopic crack occurs in the sample (between $N = 40$ and $N = 60$ cycles).

Hirschberg V., Wilhelm M., Rodrigue D., 2017. Fatigue behavior of polystyrene (PS) analyzed from the fourier transform (FT) of stress response: first evidence of $I_{2/1}(N)$ and $I_{3/1}(N)$ as new fingerprints, *Polym. Test.* 60, 343–350. <https://doi.org/10.1016/j.polymertesting.2017.04.001>.

symmetry in the stress response leading to higher even harmonics due to the macroscopic cracks. In case of a macroscopic crack, the modulus of the clockwise turn is no longer equal to the counterclockwise turn ($G(\gamma^+) \neq G(\gamma^-)$), so higher even harmonics are detected as described above.

3.3.2.2.2 Elastomers. In 2004, Lacroix analyzed the stress response of rubbery materials in strain controlled elongational fatigue tests, mainly tension/tension (T/T) at $\omega/2\pi = 5$ Hz via FT and separately investigated the higher harmonics as follows:

$$\sigma = I_1 e^{i\omega_1 t + \delta_1} + I_2 e^{2i\omega_1 t + \delta_2} + I_3 e^{3i\omega_1 t + \delta_3} + I_4 e^{4i\omega_1 t + \delta_4} + I_5 e^{5i\omega_1 t + \delta_5} \quad (12.27)$$

The main finding was that the second harmonic (I_2) increased, while the third harmonic (I_3) decreased until the end of the test. An interesting idea, which however could not be proved, was to correlate a change in the slope of I_2 (log-log plots) with crack initiation. In general, it is not clear if a macroscopic crack can be detected in I_2 for T/T test using an asymmetry argument. In T/T a crack should result in a material weakening (strength/modulus), but not necessarily in (higher) stress nonlinearity (caused by asymmetry).

Additionally, repetitions at $\gamma_0 = 15\%$ showed that the absolute values of the higher harmonics were within a 10% standard deviation and their trends were highly reproducible. Moreover, earlier failure (see the 25% curve in Figs. 12.9 and 12.10) was found to result in faster increase of the second harmonic (I_2) and higher values of the third harmonic (I_3).

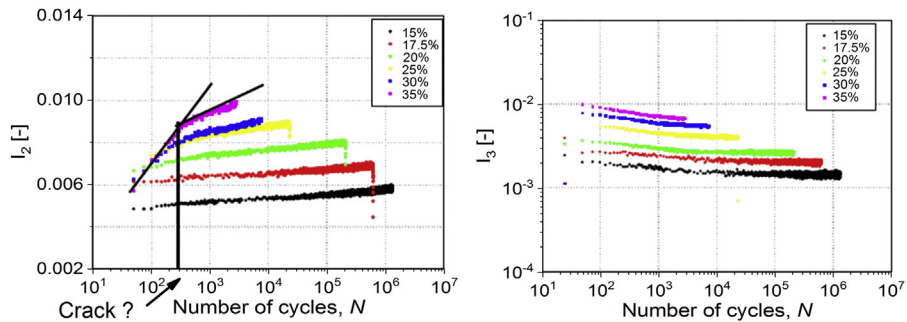


FIGURE 12.9

The second (I_2) and third harmonic (I_3) as a function of the number of cycles for a rubber at different strain amplitude (15%–35%). The values are not normalized to the fundamental harmonic (I_1). The author labeled I_2 as the first and I_3 as the second (higher) harmonics.

Adapted from Lacroix F., 2004. *Etude du comportement en fatigue des caoutchoucs synthétiques*, Ph.D. Thesis. Université de Tours (France).

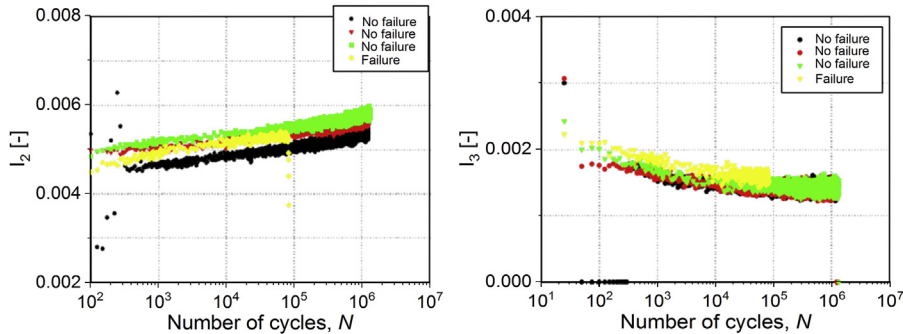


FIGURE 12.10

Reproducibility of fatigue experiments at $\gamma_0 = 15\%$ showing the absolute values of the higher harmonics at the beginning of the test and their trends as a function of the number of cycles. The author labeled I_2 as the first and I_3 as the second (higher) harmonics.

Adapted from Lacroix F., 2004. Etude du comportement en fatigue des caoutchoucs synthétiques, Ph.D. Thesis. Université de Tours (France).

4. Conclusion

This chapter gave an overview of the dynamic rheology and the mechanical properties of polymers in their solid state. Rheology fundamentals (linear dynamic, small amplitude oscillatory shear, SAOS) and of Fourier transform (FT) rheology in the viscoelastic nonlinear regime (under LAOS) have been presented. Under LAOS conditions, the polymer's material response is no longer linear viscoelastic and these nonlinearities can be quantified via FT as higher odd harmonics ($I_{3/1}$, $I_{5/1}$ etc.).

This chapter also presented the concept of mechanical fatigue for polymers. Besides the traditional standard concept of Wöhler curves, representing the number of cycles to failure as a function of the applied stress (stress controlled) or strain (strain controlled) amplitude, different approaches following the material properties as a function of time were discussed. Firstly, the polymer's viscoelasticity results in the energy dissipation during the test leading to increase in temperature. Correlations between the cumulative DE and the so-called RDEC with the fatigue lifetime were discussed in more detail. Secondly, because of the nonlinearity of polymers under large deformation, several approaches quantifying and following these nonlinear stress changes due to fatigue were explained in more details. The NVP describes the ratio of the sum of higher harmonics normalized to the fundamental one, calculating the higher harmonics via FT of the stress response. The approach is based on analyzing the higher harmonics of the stress response instead of separately. For tests in torsion, an increase of the higher even harmonics above the noise level can be correlated to the occurrence of a macroscopic crack.

Although a great deal of experimental information is available, theoretical models are still incomplete due to the complex dynamical phenomena involved. So more work in this field is under way to get better understanding and prediction for material characterization and optimization, as well as for engineers to design parts with lower safety limits in fatigue.

Glossary

A	Surface
B	Prefactor of the Wöhler correlation
C	Exponent of the Wöhler correlation
δ_1	Phase angle of the fundamental harmonic
δ_2	Phase angle of the second harmonic
δ_3	Phase angle of the third harmonic
δ_4	Phase angle of the fourth harmonic
δ_5	Phase angle of the fifth harmonic
E'	Storage modulus (elongation)
E''	Loss modulus (elongation)
F	Force
Γ	Strain
γ_0	Strain amplitude
γ^+	Clockwise strain
γ^-	Counterclockwise strain
$\dot{\gamma}$	Strain or shear rate
G'	Storage modulus (shear)
G''	Loss modulus (shear)
G^*	Complex modulus
$I_{2/1}$	Ratio of the second harmonic normalized to the fundamental one
$I_{3/1}$	Ratio of the third harmonic normalized to the fundamental one
$I_{4/1}$	Ratio of the fourth harmonic normalized to the fundamental one
$I_{5/1}$	Ratio of the fifth harmonic normalized to the fundamental one
η	Viscosity
N_f	Number of cycles to failure
ω	Angular frequency
Q	Ratio of the intensity of the third harmonic over the square of the strain amplitude
Q_0	Parameter of the intrinsic nonlinearity
R	Stress ratio
σ	Stress
s(t)	Time signal
$S(\omega)$	Signal in the frequency domain/after FT
t	Time
T/T	Tension/Tension
W_f	Cumulative dissipated energy

List of acronyms and abbreviations

DE	Dissipated energy during one cycle
FT	Fourier transform
LAOS	Large amplitude oscillatory shear
NVP	Nonlinear viscoelastic parameter
PS	Polystyrene
RDEC	Ratio of dissipated energy change
S–N curve	Stress-number of cycles to failure curve
S/N ratio	Signal to noise ratio
SAOS	Small amplitude oscillatory shear

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Magnetorheological studies of polymer nanocomposites

13

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Abstract

Recently, magnetorheological (MR) materials such as MR fluids (MRFs), MR elastomers (MREs), MR grease (MRG), and MR foams, have been considered in diverse industrial and academic areas owing to their quick response to the applied magnetic or electric fields. These characteristics aid to control over rheological properties of such materials with adjusting the strength of applied magnetic or electric fields. Among all, MREs have gained more interest because of their high research potential in the engineering field, especially for automotive application, radiation, military-related system, and rehabilitation fields. In fact, MREs mainly consist of rubber as a matrix and ferromagnetic particles in the presence of additives. The most noticeable feature of MREs is their desirable performance owing to the stability of magnetizable particles in the matrix. However, this feature is challenging because of the particle sedimentation over long-term use. Thus, to improve their magnetorheological properties, composite parameters must be controlled and scrutinized. Indeed, the matrix selection plays an important role in the development of MRE devices application by contributing to the mechanical and rheological behavior. This, in turn, would affect their design and performance. Several types of rubber, including natural rubbers, thermoplastics, and silicone rubbers, are widely used as matrix. Besides, in terms of magnetic particles, their type, size, shape, and volume fraction play significant roles on the rheological characteristics and as a consequence on their performances. Fillers or additives are incorporated into polymer-based composite materials mainly to improve processing ability, reduce the material cost, or achieve desired properties. In this chapter, MR materials and composite MREs will be introduced in detailed with emphasis on the different components and various preparation methods, which will be followed by investigation of their physicochemical and mechanical properties.

Keywords: Apparent viscosity; Carbonyl iron; Gls; Magnetorheological elastomers; Magnetorheology; Polymer nanocomposites; Sedimentation stability; Smart materials.

1. Introduction

Magnetorheological (MR) materials are smart materials that can be controlled by applying the external magnetic field. MR materials include ferromagnetic particles that are homogeneously distributed in the appropriate matrix or carrier fluid such as mineral oil, synthetic oil, water, silicone oil, and hydrocarbon oil (Kciuk and Turczyn, 2006; Hajalilou et al., 2018). The rheological properties such as yield stress and viscosity of MR materials are highly influenced by the external magnetic field. By applying the magnetic field, dispersed particles in the matrix or carrier fluid align in the direction of magnetic field and make a regular chain-like structure with a high viscosity liquid or a semisolid material (Kciuk and Turczyn, 2006; Hajalilou et al., 2017). The configuration and rigidity of this solid-state structure depend on many factors, but the most important one is a strength and distribution of applied field. The rheological behavior of MR materials is determined based on the interaction of magnetic dipoles within a particle chain. These interparticle interactions extend throughout the substance and increase the MR properties of the whole material (Jolly et al., 1996). The main advantages of MR fluids are a yield strength of up to 50–100 kPa, which is one order of magnitude higher than that of ER materials, relatively wide working temperature range (−40 to 150°C), using low voltage of 12–17 V, and insensitivity to contaminants (Wang and Meng, 1948). Without applying external magnetic field, these kind of materials show Newtonian behavior (Hajalilou et al., 2017), and in the presence of magnetic field, MR fluid represents non-Newtonian behavior which is characterized by field-dependent yield stress and an increase in viscosity. In most MR applications, the response time has the greatest importance. This time varies from 10 to 20 ms depending on magnetic circuit design. Among several magnetic materials, soft magnetic particles such as Ni–Zn ferrites or specially carbonyl iron magnetic particles owning the good ability to control the rheological ability of MR fluids due to their easy magnetization and demagnetization in comparison with hard magnetic materials (Hajalilou et al., 2016). The properties of MR fluids are mostly dependent on the magnetic particle features such as size, shape, and saturation magnetization, etc. (Shilan et al., 2016). In recent decades, due to the advances made in the field of MR technology, many researches on MR fluids and/or their effects are increased. In the following section is attempted to discuss the basis of these materials and their properties in details (Ashtiani et al., 2015).

2. Introduction to MR materials

2.1 MR fluids

To synthesize the MR fluids, iron powder is the most used popular magnetic particle materials because of their high saturation magnetization ($\mu_0 M_s = 0.2\text{T}$). One of the most important factors for MR fluid's stability is particles size; therefore the

synthesis route is very important (Phule, 1998). There are many ways to obtain uniform particle size distribution, such as chemical vapor deposition (CVD) (Wang and Meng, 1948), controlled precipitation method (Choi et al., 2005), microwave plasma technique (Wilson et al., 2004), etc. The typical diameter of the magnetizable particles used in MR fluids is about 5–6 microns. MR material suspensions easily face with sedimentation of magnetic particles with increases in their sizes.

MR fluids are increasingly becoming important in applications concerning active control of vibrations or torque transfer. Shock absorbers, vibration dampers, seismic vibration dampers, clutches, and seals are the most exciting applications of MR fluid. One of the most important and recent developments in MR fluid applications has been developed by Delphi Automotive Systems. Delphi and Cadillac developed MagneRide™ semiactive suspension system, which adjusts damping levels with the combination of MR fluid–based struts and shock absorbers (seval Genc, 2002).

2.2 MR grease

MR grease (MRG) like MR fluids is such a smart material in which its yield stress is magnetically controllable in milliseconds and with no sedimentation. Owing to its mechanical simplicity, fast response behavior, and low power behavior, these materials can work well with the demands and constrains of a vibration isolation system. In Fig. 13.1, MRG materials behavioral graphing shear stress compared with magnetic field can be seen (Zhao et al., 2011).

It is worth mentioning that the characteristics of the flow of MRG fluids in the absence of magnetic field behave in similar manner with Newtonian materials, but in the presence of magnetic field the flow divides into Newtonian (Eq. 13.1) and Bingham (Eq. 13.2) flow regions (de Castro and Liborio, 2006).

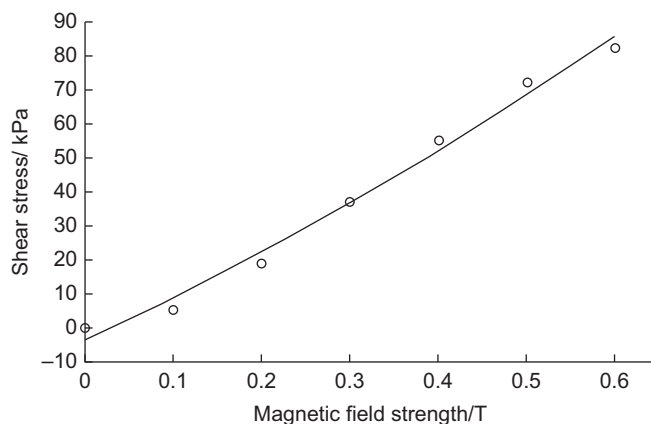


FIGURE 13.1

Shear stress change in compare with magnetic field strength (Zhao et al., 2011).

$$\tau = -\eta\dot{\gamma} \quad (13.1)$$

$$\tau = \tau_y + \eta\dot{\gamma} \quad (13.2)$$

where τ is the shear stress, τ_y is the yield stress as a function of magnetic field, η is the shear viscosity, and $\dot{\gamma}$ denotes the shear rates. Fig. 13.2 shows the differences between Newtonian and Bingham fluids.

In the rheological study of greasy materials, viscosity and shear stress of different carbonyl iron (CI) particle ratios in the presence and absence of magnetic fields have been investigated. What is clear is that by increasing the CI particle percentage and magnetic field, the viscosity of the MRG fluids increases. Fig. 13.3 shows the effect of CI particles percentage on the viscosity of MRG in the presence of 0.7T magnetic field. This increase in viscosity is because of strong interaction between CI particles, which can rearrange the solid-like structure in the presence of critical density of magnetic field.

In fact, the reason why MRG shows better results in comparison with MR fluids is due to their being softness as the medium and the better alignment of particles in greasy mediums. Table 13.1 shows more details about magnetorheological properties of MRG fluids (Mohamad et al., 2016).

2.3 MR foam

Porous materials, such as the sponge, sintered metallic felt, or fabric, are widely used and designed to solve the following problems, such as the seal, required volume, and cost of the MR damper. Metal foam has a very high porosity, that is, nearly 75%–95% of the volume of the material. Metal foam is mainly made of metal usually nickel (Ni), copper (Cu), iron (Fe), and aluminum (Al). The main advantages of

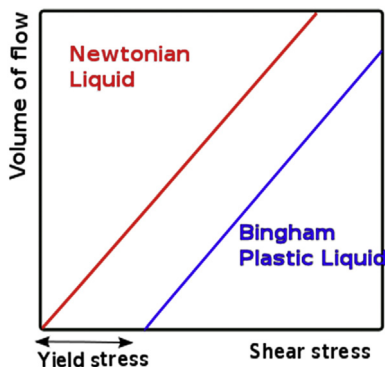
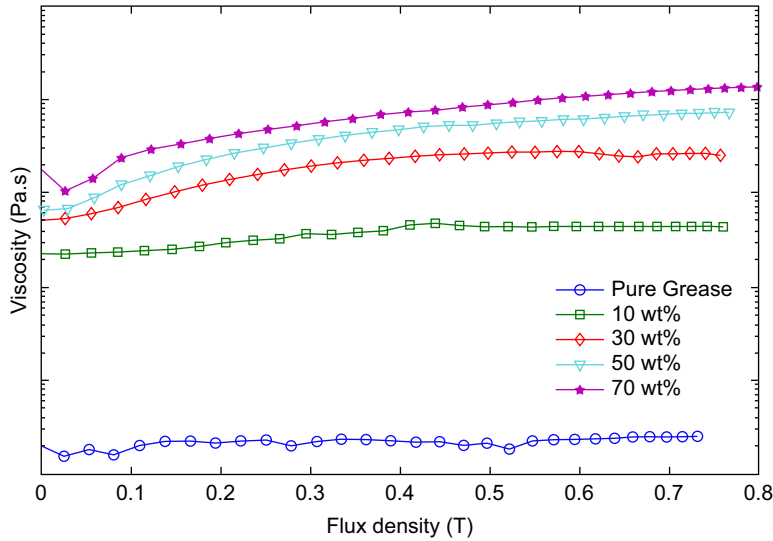


FIGURE 13.2

Bingham Plastic flow as described by Bingham.

**FIGURE 13.3**

Viscosity of MR grease as a function of magnetic flux density (Mohamad et al., 2016).

these foams are the high porosity and stability with low weight. There are many shortcomings for designing MR foam materials by using the sponge, such as its stiffness and durability, which will shorten the life of dampers. Based on the design of MR damper, the metal foams will satisfy the following: (1) The size of the particles; if they are too big, the capillary effect will be unobvious and MR fluid will leak from the damper, and if they are too small most of the magnetic particles will be blocked. (2) The high porosity should be suitable to store MR fluid. (3) The bigger rigidity will be necessary to resist wear and distortion (Liu et al., 2011). In the case of polymeric MR foams, typically the matrix material used is open-celled polyurethane foam. Some basic properties of open-celled polyurethane foam are listed in Table 13.2 (Kim et al., 2016).

In Table 13.2, λ is the anisotropy parameter, ρ^* is the density of the foam, E^* is the foam axial modulus, σ_{11} is the initiation stress, and σ_{1P} is the propagation stress. ρ and E are the density and axial moduli for the base material, respectively. Their values are 2.04 and 69 MPa, respectively. The MR sponge cell consists of MR fluid and open-celled polyurethane, as shown in Fig. 13.4 (Kim et al., 2016).

Various operating electrical currents and shear rates are influencing the response time of the metal foam MR dampers. MR fluids needed in the metal MR foam dampers are much less than traditional ones. Compared with the sponge MR dampers, metal foam MR dampers have advantages of durability, longer life, and better permeability (Yan et al., 2013).

Table 13.1 Key parameters of MR G with different magnetic particle content and current (Mohamad et al., 2016).

Sample	Current, A	Shear rates, 1/s	Shear viscosity, Pa·s	Shear stress, Pa	Dynamic yield stress, Pa
MRG-10	0	2,000	0.0012	25	1.4
	1	2,000	0.001	21	64.7
	2	2,000	0.0036	7.2	475.5
	3	2,000	0.0165	33.1	379.8
	4	2,000	1.5558	3112.1	1893.5
	5	2,000	1.8985	3797.3	2284.3
MRG-30	0	2,000	0.0009	1.7	3.1
	1	2,000	0.25164	503.3	802.0
	2	2,000	4.2906	8581.3	4059.8
	3	2,000	6.6636	13,339	9813.2
	4	2,000	7.7965	15,976	10946.0
	5	2,000	2.1921	17,237	12018.0
MRG-50	0	2,000	2.1921	4384.2	3549.2
	1	2,000	5.5950	11194.0	9268.9
	2	2,000	9.7619	19537.0	12507.0
	3	2,000	15.3160	30465.0	15978.0
	4	2,000	16.9490	32642.0	18678.0
	5	2,000	23.8090	40432.0	27318.0
MRG-70	0	2,000	6.0210	12424.0	6060.0
	1	2,000	8.8785	17764.0	7677.4
	2	2,000	16.1230	31528.0	20520.0
	3	2,000	30.9380	46933.0	33696.0
	4	2,000	53.4870	60592.0	46384.0
	5	2,000	76.6170	68365.0	53726.0

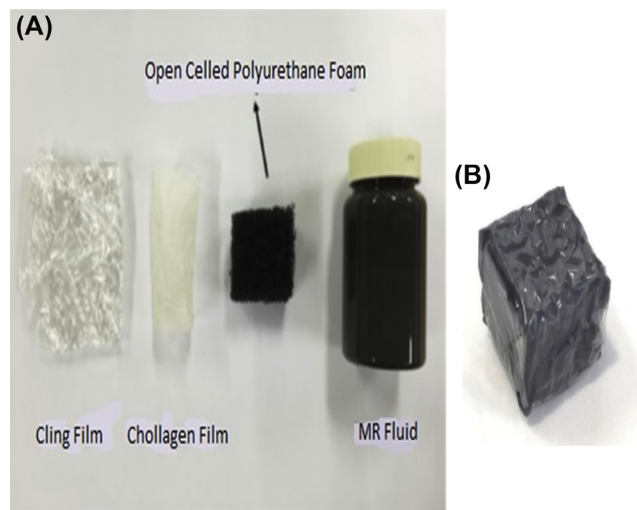
3. Polymer-based magnetorheological nanocomposite materials

3.1 MR polymer components

One of the new and popular composites, which has poor particle–matrix interaction, is MR elastomers. MR elastomer materials consist of micron-sized magnetic particles distributed in a nonmagnetic elastic matrix such as polyurethane (PU), natural rubber, silicone rubber, or other elastomers. In polymer matrix, using excessive content of magnetic particles causes aggregation or bubble defect. Therefore, by enhancing the interfacial interaction among the matrix and particles, it causes improvement in the mechanical strength, durability, stability, and other macroscopic

Table 13.2 Properties of open-celled polyurethane foam (Kim et al., 2016).

Property	Value
λ	1.256–1.281
$\frac{\rho}{\rho^*}$ (%)	2.36–2.44
$\frac{E}{E^*}$ (%)	0.200–0.215
(kPa)	4.9–5.8
σ_{1P} (kPa)	4.8–5.7

**FIGURE 13.4**

Manufactured MR sponge cell: (A) components of MR sponge cell, and (B) assembled sponge cell (Kim et al., 2016).

properties (Yu et al., 2017). The common problem of MR fluids is settling the ferromagnetic particles which tend to reduce the efficiency of devices. One of the ways to solve this problem is to use solid base materials such as thermosetting polymers or elastomers, which can provide a stable medium for the particles. In addition, one of the other most important differences between MR fluids and MRE is their field of application. MR fluids are operational in postyield regime and MREs are used in preyield stress region.

3.2 Matrix

Best durability can be achieved by MR polymers because magnetic particles have less sedimentation in polymer matrix. On the other hand, the potential problems

in MRE materials are oxidation, stiffness, polymeric hysteresis, and durability. In this case, there are two issues that need to be considered: (1) the stiffness of the MRE should not be high and (2) oxidation of the particles must be prevented.

Oxidation happens when the MR plastomer (MRP) is exposed in air. Oxidation can be reduced by particles surface treatment. Bridging among carbon particles because of surface coating is another concern. To prevent these effects, silicone and polyurethane-based elastomers are good candidates because of their thermooxidative, chemical resistance, and mechanical properties (Guo et al., 2013). One of the most widely used materials as matrix is heat-curable silicone rubber in both room and high temperatures. The conventional method for fabricating the MR polymer-based materials is molding. The other manufacturing method is 3D printing, using layer-by-layer printing technique to produce the final product. Fig. 13.5 shows the concept of 3D printer to producing the MR polymer materials (Bastola et al., 2017).

3.3 Magnetic particles

For the MR applications, the most widely used magnetic particles are carbonyl iron (CI) particles because of their high effectiveness under external magnetic field, making the chain-like structure, which improves the rheological effects, e.g., yield stress of the materials. For manufacturing the iron-based materials and alloys, there have been suggested several methods: decomposition of iron pentacarbonyl, sol-gel ultrasonic decomposition of organometallic precursors, plasma torch synthesis, electric explosion of metal wires, chemical reduction and precipitation, and laser ablation. Some other alloys such as Fe-Co materials have higher saturation

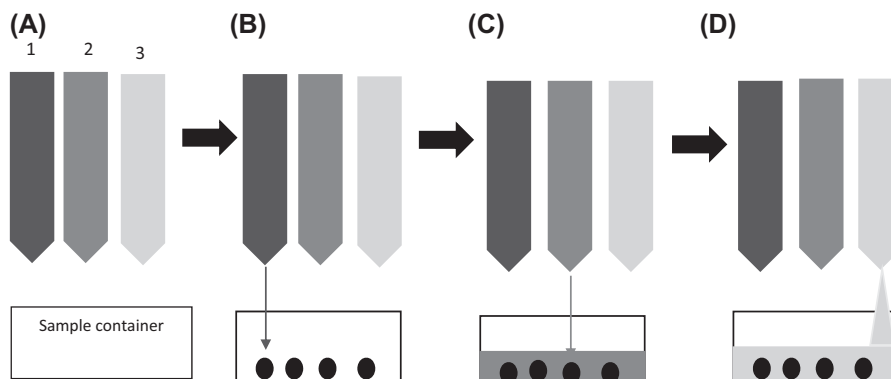


FIGURE 13.5

Schematic diagram of single-layer printing in the H-MRE fabrication process. (A) Three printing components: (1) MR fluid cartridge, (2) elastomer resin cartridge, (3) UV curing unit. (B) Printing of MR fluid. (C) Dispensing of elastomer resin, and (D) Curing with UV light (Bastola et al., 2017).

magnetization ($\sim 2.4T$), but cost and unavailability make them undesirable. Ferrimagnetic materials such as manganese–zinc ferrite and nickel–zinc ferrite have lower saturation magnetization, thus exhibiting lower maximum yield stress (Wilson et al., 2002). The main problem in the use of magnetic particles in MR application is their large densities (sedimentation) and rigid surface (abrasion). To solve these problems, using dispersing of nano- and micron-sized particles in the fluid or carrier has attracted attention (Hajalilou et al., 2016). Another common way is to synthesize the composite particles coated by polymeric materials (Zhou and Jiang, 2004). Poly (methyl methacrylate) (PMMA) (Guo et al., 2013), polyurethane (PU) (Seo et al., 2016), and polystyrene (PS) (Seo et al., 2016) are examples of these polymeric materials.

Several important factors for CI particles as a dispersed constituent in MR fluids must be considered: volume fraction, particle size, and shape. Usually the volume fraction of the magnetic particles is around 0.3–0.5 volume fraction of the matrix. Particle size as another important factor has the great influence on the rheological properties of “on or off” states of MR fluids. Particles with size bigger than $>10\text{ }\mu\text{m}$ have the higher yield stress, but by increasing the particle size the particles settling increase and form less stable MR fluids (Wilson et al., 2002).

3.4 Additives

The big issue in using of magnetic particles in MR materials is their sedimentation, which is due to large-density mismatch between magnetic particles (7.68 g/cm^3 , for CI) and suspending medium. Different techniques are used to avoid sedimentation of magnetic particles in MR fluids, such as polymer coating on magnetic particles to reduce the density mismatch. Coating process has been reported as a complex method because of various factors affecting coating thickness such as temperature, molar ratio, or reaction time. The other new technique which reported as a dominate method is use of additives such as thixotropic agents, surfactants, or fillers, which can intercept the physical contact of magnetic particles (Hajalilou et al., 2016).

Carbon-containing materials such as 1D carbon nanotubes (CNTs) and carbon microfibers (CFs) are the new generations of additives to achieve high shear strength, bending strength, stiffness, and durability (Xu et al., 2017). Generally, using additives in addition to the surface protection provides stability and extends the operating life of the system (Hu et al., 2006).

4. Introduction to variety of MRP nanocomposites and material

4.1 MR elastomers

MR elastomers are a new generation of MR fluids where the matrix is a solid elastic polymer. Their characteristics include having controllable magnetic field dependency and stable performance without sedimentation of magnetic particles problem,

which exists in MR fluids. MREs have sensitive response to magnetic field and less than 10 ms as the time of response. Mainly, MR elastomers are composed of magnetic particles and elastic polymer matrix. Usually magnetic particles are carbonyl iron particles and polymer matrix as reported in literature including soft silicone elastomers, poly(vinyl alcohol), gelatin, hard natural rubber, and polyurethane sealant (Wu et al., 2010). Two kinds of common matrices that are used in MR elastomers are silicone rubber and natural rubber. Silicone rubber has several advantages such as, firstly, simply processed from liquid precursors with low viscosity and, secondly, high relative RM effect for the low zero-field modulus. However, it may not be so useful in practical applications because of its low strength and reduced fatigue life after loading high volume of magnetic particles. For natural rubber, it has good properties as MREs, but its high viscosity makes magnetic particles difficult to form chain-like structure under a magnetic field (Wang et al., 2006). The field-dependent MRE properties are featured as modulus rather than yield stress. MREs have a more stiffness-related behavior rather than the damping performance of MR fluids (Li and Zhang, 2010). MREs and MR fluids are different in operating ranges. The main area of application of MREs are vibration absorbers (Kukla et al., 2017), variable stiffness suspension bushing, and tunable spring elements (An et al., 2017).

4.2 MR plastomers (MRPs)

As discussed above, MR fluids (MRFs) are the first kids of MR materials, but because of magnetic particle sedimentation as negative point, MRFs have found practical limitations. Thus, the MR elastomers have been developed to overcome MRFs awful point. However, MR elastomers face many challenges in the practical applications because of the weak MR features by the hard nature of the polymer matrix. For this purpose, new kinds of plastic materials with a soft matrix feature, due to low cross-linking density of the carrying matrix, have been developed (Xuan et al., 2015). MR plastomers, unlike MREs, have stability, rapid response, and high MR effects. Recently some properties of MRPs such as compression performance, shear performance, creep and recovery, and shear-dependent electrical performance have been intensively investigated (Xu et al., 2018). In plastomer-based MR materials, the ordered microstructures, which appear in the presence of magnetic field, will be kept for a period of time while the external magnetic field had switched off or removed (Liu et al., 2014).

4.3 MR gels

Using polymeric gels as the MRF medium like other materials is to overcome the sedimentation of magnetic particles. The main difference among this type of materials and other polymeric or nonpolymeric materials is being able to control

the off-state viscosity, and the stability of the system can improve by precipitation of the polymeric gels on the surface of the magnetic particles (Guo et al., 2013). Other advantages of MR gels are tended to have liquid-like behavior which imitates the MRF behavior with higher yield stress and lower particle settling. According to the mentioned features, MR gels have a great potential to replace MRFs in some applications such as dampers, MR isolators, MR brakes, and vibration control (Xu et al., 2013). An important factor for MR gel materials is dynamic mechanical performance. This is because MR gel devices often work in dynamic modes. Ideal MR material should have both a high magneto-induced storage modulus and a high relative MR effect (Yang et al., 2016).

4.4 Preparation methods of MR polymer materials

4.4.1 MREs and MRPs

MREs as polymer matrix composite (PMC) consist of distributed micro- or nano-sized ferromagnetic particles such as CI in polymeric matrix; here the polymer matrix consists of elastomers. The preparation of MREs has three steps: (1) blending, (2) preforming, and (3) forming and curing (Stepanov et al., 2012).

Magnetic particles of MREs can be classified according to magnetic properties such as (1) soft magnetic particles, (2) hard magnetic particles, (3) magnetoactive particles, and (4) magnetic shape memory (MSM) particles (Boczkowska et al., 2012). For example, $\text{BaFe}_{12}\text{O}_{19}$ or $\text{SrFe}_{12}\text{O}_{19}$ is used as hard magnetic filler in some MREs (Dishovsky et al., 2001). Magnetostrictive particles such as Terfenol-D alloys are used in MREs. Terfenol D is the most famous alloy of magnetostrictive materials with large magnetostriction (Xu et al., 2013; Feuchtwanger et al., 2008), and Ni–Mn–Ga particles are example of MSM materials (Scheerbaum et al., 2007). According to previous reports, soft magnetic particles, mainly iron, CI, cobalt, and their oxides, are used as filler in MREs (de Vicente et al., 2002; An et al., 2003; Lokander et al., 2003).

4.4.2 Fabrication of MREs

Curing process is used for preparing polymers in MREs as polymer matrix. During the process, polymeric materials (e.g., silicone rubber) are mixed with CI and various other chemical additives are added to improve their mechanical properties (Boczkowska et al., 2012).

Depending on the polymer used, prepared mixture is cured at different temperatures. Silicone Elastosil can be vulcanized by combining the resin/hardener at room temperature (Kallio et al., 2007), or in the presence of polyurethane (PU) matrix, PU-CI composite cured at 120°C (Guo et al., 2013).

The spatial distribution of the particles is determined during curing process. In the presence of a magnetic field during curing, the obtained elastomer has anisotropic, oriented structure, consisting of chains of particles. Magnetorheological

elastomer cured without the magnetic field allows to receive isotropic structure (Kallio, 2005).

Guo et al., 2013 used PU with a hard segment as matrix for MREs. Typically, approach to synthesize PU MREs is the one-step polycondensation process. CI was mixed with preheated polytetramethylene (PTMEG) and diisooctyl phthalate (DOP) (100°C) via ball milling for 30 min. The prepared PTMEG/DOP/CI mixture was heated at 100°C before addition of 4,4'-methylene-di(phenylene isocyanate) (MDI) and 1,4-butanediol (BDO). The obtained viscous prepolymer was transferred into a preheated hot O-ring mold in the presence of an oriental magnetic field for 1 h.

Ge et al. (2013) synthesized MREs by mixing of natural rubber (NR) as the matrix and rosin glycerin ester as another part of the matrix to improve wettability and dispersibility of carbonyl iron particles. For preparation of MR composite, first, a certain amount of NR and rosin glycerin ester was mixed homogeneously by a two-roll mill. In the following, carbonyl iron particles with average size of 7 μm were added to the previous-prepared rubber compound. This mixture was poured into mold under a pressure of 20 MPa in the presence of an external 1300 mT magnetic field. Under these conditions, the mold was heated at 80°C for 15 min. Once the magnetic field was removed, the temperature was increased to 153°C and heated for 20 min.

Yang et al. (2013) reported that addition of silicone carbide (SiC)-strengthened to typical carbonyl iron and natural rubber CI/NR MREs can affect viscoelastic performance of MREs. They studied the effect of different size and weight content of the SiC particles on the viscoelastic properties of CI/NR MREs. Addition of SiC-strengthened to MREs leads to higher G_0 , ΔG , and damping property relative to the sample without SiC particles. The optimum value of the SiC-strengthened content in composite compound was 3.2 wt%.

Yu et al. (2015) prepared polyurethane-epoxy resin graft interpenetrating polymer networks (PU/EP IPNs) by mixing of g-PU, DBP/CIP dispersion and the mixture of EP/DMP-30. g-PU obtains by mixing of castor oil and methylene diphenyl diisocyanate (MDI) which was heated at 80°C for 15 min. In another study, Ju et al. (2012) synthesized MREs via mixing of three ingredients such as: carbonyl iron particles (CI), silicone rubber (SR) and ammonium bicarbonate (NH_4HCO_3). Firstly, NH_4HCO_3 and SR were swallowed. In the following CI was added to mixture and stirred for 10 min. After remove of the air bubble of the obtained mixture in a vacuum oven, the homogeneous compound was transferred to an aluminum mold and was cured at 100°C for 2 h without external magnetic field. During curing, NH_4HCO_3 decomposed into NH_3 , CO_2 and H_2O .

In Liu et al. (2013) and Xu et al. (2011) studies, toluene diisocyanate (TDI) and polypropylene glycol (PPG) were mixed together into flask and stirred at 70°C for 2 h. In the following, 1,4-butanediol (BDO) was added to the mixture and temperature was decreased to 65°C. After stirring for 1 h under this condition, stannous octoate was added into flask.

Carbonyl iron particles were added to obtained elastomer matrix and maintained at room temperature for 72 h. Xu et al. (2011) reported that MRPs have higher magnetorheological performance than that of MREs under similar condition.

In the following, the preparation methods of MR polymer materials based on elastomer will be discussed. It is worth mentioning that major differences between polyurethane based MREs and MRPs is: preparing of elastomer is carried out at room temperature while the MREs polyurethane matrix preparation is at temperature about 70–110°C.

Zhao et al. (2017) synthesized polyurethane based MRPs. Firstly, they mixed TDI and PPG with molar ratio of 3:1 and in the following they added BDO and ethyl alcohol to the mixture. By increasing the viscosity of mixture, the reaction was stopped. Carbonyl iron as soft magnetic materials and NdBFe as hard magnetic materials were added and were dispersed well into polymer matrix.

TDI and PPG and diethylene glycol (DEG) were used as precursors and carbonyl iron particles were added to obtain polymer as magnetic particles.

Pang et al. (2015), added graphite particles into MRP due to enhance the electroconductivity of the final MRPs. Also, they expressed relation between content and size of graphite particles and resistance of MRP. It was found that electrical resistance of the sample without graphite was approximately 10,000 times higher than that of the sample with 15 wt% of graphite particles.

4.4.3 Magnetorheological polymer gels (MRPGs) & magnetorheological gels (MRGs)

Magnetorheological gels are analogous materials to magnetorheological fluids and magnetorheological elastomers. They are also composed of micron-sized magnetic particles but unlike MRFs and MREs, the magnetic particles in magnetorheological gels are dispersed in a gel. This feature of MRG helps intrinsically to overcome the distinct shortcomings shown by magnetorheological fluids e.g., the settling of the magnetic material in time due to the density mismatch and the small response ratio that magnetorheological elastomers shows due to limited movement of the particles within a polymeric matrix.

MRGs are conventionally prepared by dispersing the magnetic particles within a fluid that can be gellated with gelator agents (i.e., water, polymers, etc.). A gel is obtained at room temperature and upon heating or cooling it melts to obtain a fluid: this is a fully reversible process. A feature of MRGs is that they respond to more than just one stimulus: i.e., magnetic field and temperature or pressure. These effects can be used for applications that depend on certain temperature ranges. This will avoid settling of the particles while it becomes liquid at high or low temperature.

MRPGs & MRGs consist of three main ingredients: (1) the cross-linking agent (2) magnetic particles (e.g., carbonyl iron), and sometimes use from, and (3) catalyst (e.g., platinum flake) to accelerate and improve of synthesis of MRPGs matrix in presence of silicone gels (Pang et al., 2015).

4.4.4 Fabrication of MRPGs & MRGs

Frshad et al. (2005) used silicone gels as filler, platinum as catalyst and carbonyl iron particles in the synthesis of MRPGs. According to trial and error procedure, a weight ratio of silicone gels to platinum catalyst is selected 1.5. Particle size of used CI is $3.8\ \mu\text{m}$ with 80 wt% in every sample. Carbonyl iron, silicone gels and platinum were mixed together according to noted amounts and obtained mixture was transferred to cylindrical molds with nominal dimension ($D \sim 13.5\ \text{mm}$ and $h \sim 13.5\ \text{mm}$). The molds were maintained at room temperature for curing for 24 h.

Xu et al. (2013) for the synthesis of polymer matrix first, toluene diisocyanate (TDI) and polypropylene glycol (PPG-1000, $M_n = 1000$) mixed together into three-necked round bottom flask under stirring at 70°C for 2 h. After cooling the prepared mixture to 40°C , the dipropylene glycol was added to flask as a chain extender. The mixture stirred under this condition for 20 min. In the following, 1-methyl-2-pyrrolidone with different weight ratio to the obtained mixture and carbonyl iron (70 wt%) particles were added to the matrix (polymer gels and solvent). According to reference, Fig. 13.6 shows the preparation process of the MR gels.

Wilson et al. (2002) were used polyurethanes and silicone polymer system as the matrix in MRPGs sample. In the first sample were used and in the second sample was used. For the formulation of polyurethanes, polyols (polyethylene glycol and polyether polyol) and isocyanates were used.

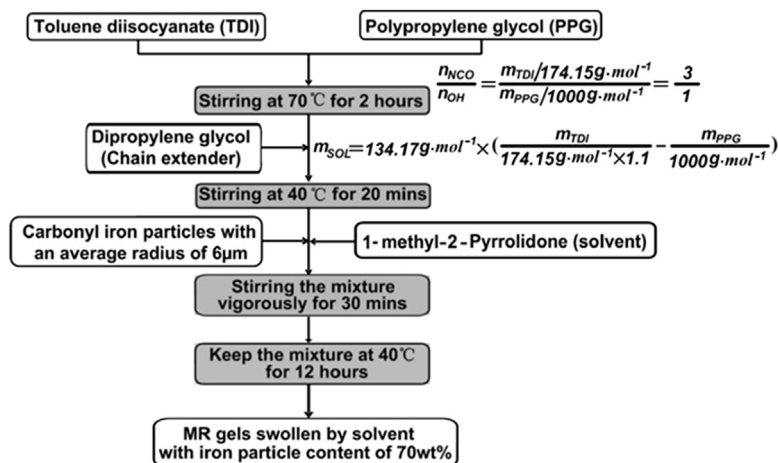


FIGURE 13.6

The preparation process of MR gels swollen by solvent in different weight fractions. n_{NCO} is the mol of the $-\text{NCO}$ group while n_{OH} is the mol of the $-\text{OH}$ group, m_{TDI} , m_{PPG} , and m_{SOL} represent the weight of toluene diisocyanate, polypropylene glycol, and dipropylene glycol, respectively. The weight of reactants can be calculated according to the formulas in the scheme (Xu et al., 2013).

For the synthesis of second sample by using silicone gels, vinylpolydimethylsiloxane (VPDMS) as resin and platinum as catalyst and dimethylmethylhydrogenopolysiloxane (DMMHPS) as hydride crosslinker were used. After polymeric matrix preparation, carbonyl iron with particle size of 6 μm was dispersed into polymeric matrix.

Fuchs et al. (2004), synthesized two polymeric matrix: (1)- Polyurethane gels and (2)- Silicone gels and in the following, the obtained polymer system was added to the hydrocarbon oil or silicone oil. Carbonyl iron particles (79.5–84.5 wt%) were suspended in the prepared carrier fluid from previous step. The mixture was stirred at 1000 rpm at ambient temperature for 10 min. They illustrated that MRPGs can control the off-state viscosity and particle settling.

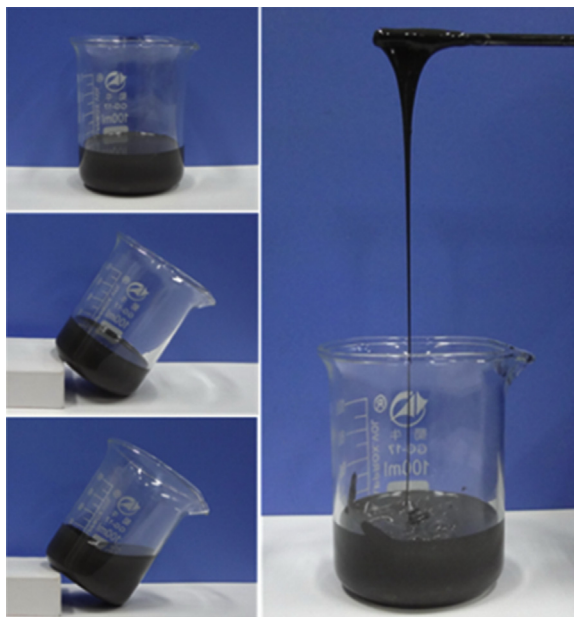
Fuchs et al. (2005) synthesized cross-linked copolyimide as matrix. For this aim, they used 4,4'-(4,4'-isopropylidene diphenoxy)bis(phthalic anhydride), 4,4'-methylenedianiline (MDA) in the solvent octyl-2-pyrrolidinone. The rate of cross-linked can be controlled by the stoichiometric ratio of diaminobenzonic acid to 4,4'-methylenedianiline. Then carbonyl iron (81 wt%) was dispersed in cross-linked copolyimide (CCPI) gel and mixed at 400 rpm for 30 min. For the completing the synthesis of MRPGs sample, the obtained mixture was stirred at 1200 rpm at room temperature for 24 h. In the following, MRPG sample were heated to 70°C for 24 h in order to do micromechanical tests. By increasing of temperature, carbonyl iron particles redisperse among polymer matrix, and in the following obtained gel mixed with polymer carrier medium (17 wt%), additives were used to stabilize MRPG. It was found that the viscosity of MRPGs is lower than that of typical MRF, which can be controlled by the concentration of cross-linked polyimide in the MRPGs structure.

Hu et al. (2006) used supermolecular polymer gels as matrix. For the preparation of MRPGs, carbonyl iron particles were dispersed in supermolecular polymer gels which were mixed with N-octyl-pyrrolidone. Metal coordination bonding between the functional group terpyridine and zinc ion (Zn^{2+}) were prepared by supermolecular magnetorheological polymer gel (SMPRG) network.

Yu et al. (2014), used polyurethane as matrix of MRPG. Homemade polyurethane was synthesized by mixing of castor oil (CO) and diphenylmethane diisocyanate (MDI) at 80°C. Molar ratio of MDI and CO was calculated by following formula (Eq. 13.3):

$$\frac{n_{\text{OH}}}{n_{\text{NCO}}} = \frac{m_{\text{CO}}/\text{g/mol}}{m_{\text{MDI}}/250 \text{ g/mol}} \quad (13.3)$$

Where n_{OH} is the mole of $-\text{OH}$ group, n_{NCO} is the mole of $-\text{NCO}$ group, m_{CO} is the weight of CO and m_{MDI} is the weight of MDI. Carbonyl iron particles were mixed with synthesized polyurethane. Simultaneously stannous ocoate was added to mixture by dropwise as catalyst. The mixture maintained in an oven to vulcanize at 80°C for 1 h. Fig. 13.7 shows an example of prepared MR gel materials.

**FIGURE 13.7**

Photographs of MRG samples (Yu et al., 2014).

5. Physical, chemical and mechanical properties of MRP

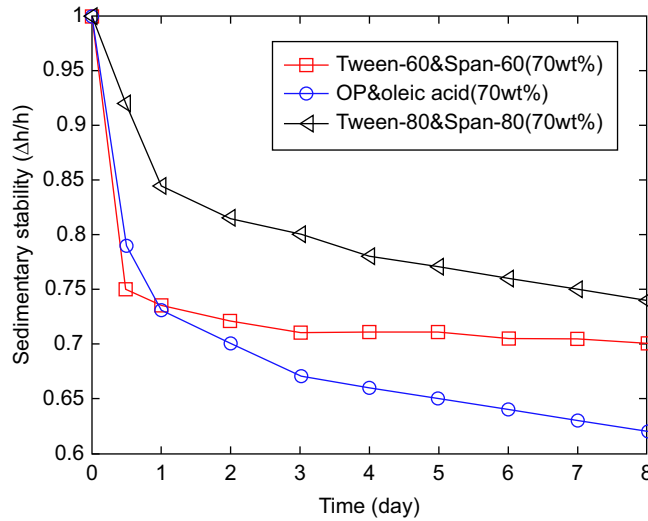
5.1 Particles stability and size distribution

As mentioned at previous parts, in order to overcome the sedimentation of the magnetic particles in the medium of the MR fluids, coating polymers on magnetic particles surface, using additives or surfactants have been recommended. Among additives and as it reported by Zhang et al., adding tween 80 (polysorbate 80) and span 80 had better results in improving of sedimentary stability than that of some other additives like olefin polymer (OP) or oleic acid as it is indicated in Fig. 13.8. Particles settling ratio can be determined by measuring the rate of formation of clear fluid layer on top of the fluid.

In addition, the optimum particle size with highest sedimentary stability and slowest sedimentary velocity was found to be 2.73 μm based on the following Eq. (13.4) (Zhang et al., 2009).

$$V = \frac{(\rho - \rho_0)gd^2}{18\eta} \quad (13.4)$$

Where V is the sedimentary velocity of particles in carrier fluid; ρ and d are the density and radius of the particles, respectively; ρ_0 and η are the density and viscosity of the carrier fluid, respectively; g is the gravitational constant.

**FIGURE 13.8**

Sedimentary stability versus time (Zhang et al., 2009).

According to López-López et al. (2005), in order to study the sedimentation behavior in suspensions contains iron particles dispersed in the fluid, the following dimensionless increment Eq. (13.5) can be used:

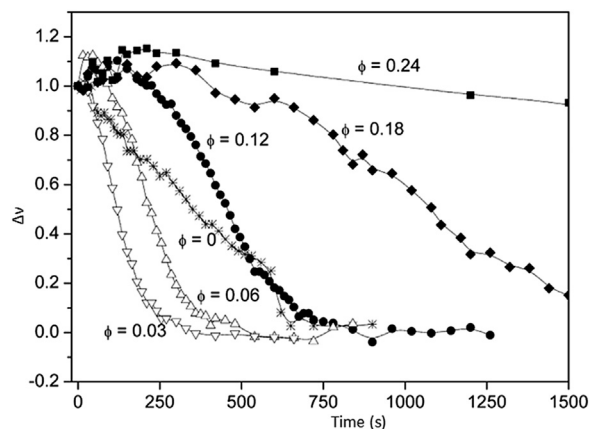
$$\Delta v \approx \frac{\Phi(t)[1 - \Phi(t=0)]}{\Phi(t=0)[1 - \Phi(t)]} \propto \frac{\Phi(t)}{1 - \Phi(t)} \quad (13.5)$$

where $\Phi(t)$ is the instantaneous iron volume fraction in the suspension surrounded by the sensing coil.

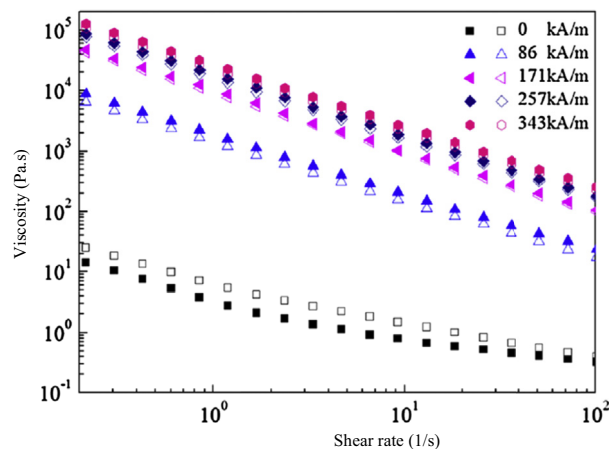
Fig. 13.9 shows sedimentation behavior, presented as Δv versus time, for iron/magnetite suspensions. Magnetite volume fraction ranges from 0% to 24%. Small increase of Fe_3O_4 concentration ($\phi = 0.03$ and 0.06) implies an increase in sedimentation rate as compared with ($\phi = 0$). This can be due to an irreversible aggregation between iron particles in the absence of Fe_3O_4 nanoparticles. By further increase in the volume fraction of magnetite nanoparticles the sedimentation rate decreases. This can be due to increase in viscosity of the ferrofluid carriers.

5.2 Shear stress and viscosity behavior

According to Bae et al. (2017) report, Fig. 13.10 shows the characteristics of shear viscosity of pure CI and CI/MCC (microcrystalline cellulose) based MR suspensions as a function of shear rate ranging from 0.2 to 100 (1/s) at various magnetic field strength. As is obvious from the figure, shear viscosity of the pure CI-based MR fluid is lower than that of CI/MCC-based MR fluid at zero magnetic field strength due to

**FIGURE 13.9**

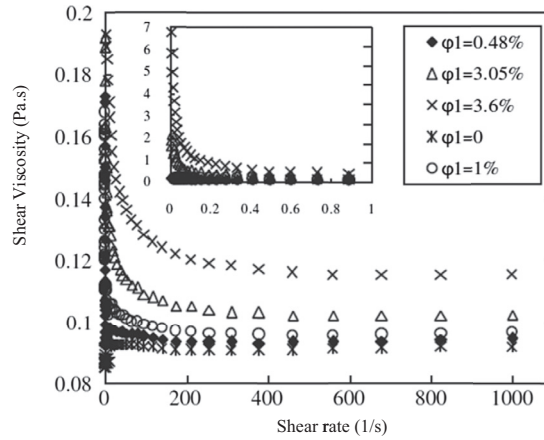
Dimensionless increment of the induced potential (Δv) versus time, for iron suspensions (initial iron volume fraction $\Phi = 0.1$) with different ferrofluid carriers. The magnetite volume fraction of the ferrofluids ϕ is indicated (López-López et al., 2005).

**FIGURE 13.10**

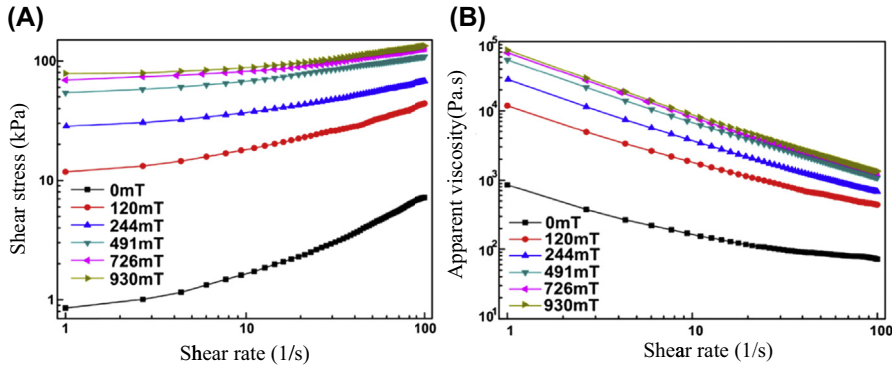
Shear viscosity data as function of shear rate from 0.2 to 100 s^{-1} for pure CI (closed) and CI/MCC (open) under various magnetic field strength (Bae et al., 2017).

the addition of MCC particles. The difference in shear viscosity can be an important factor in controlling the properties of the MR fluids.

Fig. 13.11 which is related to research of Zafarani-moattar, shows the shear viscosity – shear rate dependence for pure PEG and $\text{Fe}_3\text{O}_4/\text{PEG}$ fluid at different concentrations. This figure indicates that by increasing the volume fraction of the Fe_3O_4 in the constant shear rate, shear viscosity increases. From the other hand,

**FIGURE 13.11**

Shear viscosity versus shear rate for nanofluid of Fe_3O_4 in PEG at different volume fraction of Fe_3O_4 nanoparticle, ϕ_1 (Zafarani-Moattar and Majdan-Cegincara, 2013).

**FIGURE 13.12**

Shear stress (A) and apparent viscosity (B) as a function of shear rate for MR gels with 30 wt% of solvent content under different magnetic fields (Xu et al., 2013).

by increasing the shear rate shear viscosity increases (Zafarani-Moattar and Majdan-Cegincara, 2013).

Yangguang Xu's research on soft magnetorheological polymer gels is another example to see the effect of magnetic particles on the flow behavior of MR polymer gel. Figs. 13.12A and B. show the shear stress and apparent viscosity of MR gels as a function of shear rate at different magnetic fields. The yield stress increases by increasing the magnetic field (Fig. 13.12A). This flow behavior can be described by Bingham equation as follows:

$$\tau = \tau_y + \eta\dot{\gamma} \quad (13.6)$$

where τ and $\dot{\gamma}$ refer to the shear stress and shear rate, respectively and τ_y is the field dependent dynamic yield stress and η is the plastic viscosity (Xu et al., 2013).

To investigate the effect of some additives on rheological properties of MR fluids, Pu's research can be consulted (Pu et al., 2006). The effect of polyvinylpyrrolidone (PVP) and Carbon nanotube (CNT) on rheological properties of iron-based MR fluids was studied. Fig. 13.13 shows the effect of PVP on the apparent viscosity of MR fluids. It is obvious that apparent viscosity increases by enhancing the external magnetic field intensity. Although addition of PVP increases the original apparent viscosity in zero external magnetic field intensity. From the other side, addition of PVP does not change the uptrend of the apparent viscosity by increasing the external magnetic intensity.

Fig. 13.14 shows the effect of CNTs on magnetorheological properties of MR fluids. As it can be found from the figure is: in Zero magnetic field the original apparent viscosity increases by increasing the CNT contents. Also, the strongest effect by adding CNTs occurs in high external magnetic field intensities. This is because the magnetizable particles creates solid like chains structure and CNTs are fixed in different chains.

5.3 Thermal property

Thermo-gravimetric analysis (TGA) and differential thermal gravimetric (DTG) are the most common techniques to evaluate the thermal stability and estimate the approximate amount of coated polymeric materials on the magnetic particles of

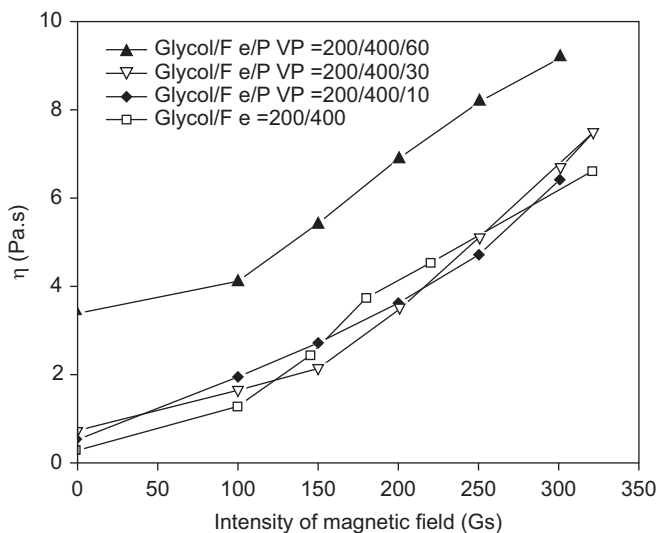
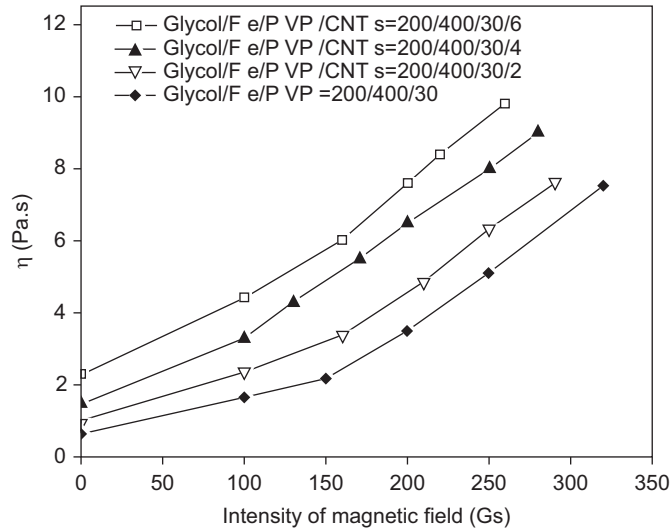


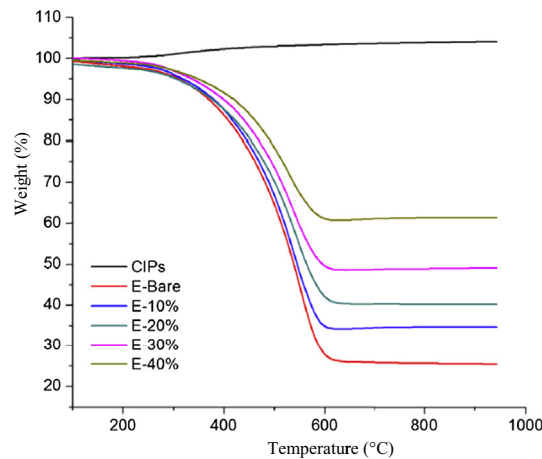
FIGURE 13.13

Effects of PVP contents on magnetorheological properties of the iron-based MR fluids (Glycol/Fe/PVP ($M_n = 30,000$) = 200/400/x) (Pu et al., 2006).

**FIGURE 13.14**

Effects of CNT contents on magnetorheological properties of the iron-based MR fluids (Glycol/Fe/PVP ($M_n = 30,000$)/CNTs = 200/400/30/x) (Pu et al., 2006).

MR fluids. Weight losing in the TGA shows the degradation coating layers and any slight increase in weight is due to oxidation of particles. Fig. 13.15 depicts the TGA analyses of silicone rubber based elastomer MR fluid which is attributed to I. Perales-Martínez et al. research. As it is shown from the figure, the carbon iron particles (CIPs) have a slight increase in weight, which is due to oxidation of magnetic particles. The most losing in weight is attributed to the bare sample (silicone)

**FIGURE 13.15**

TGA thermograms of MRE with different contents of CIPs (Perales-Martínez et al., 2017).

rubber matrix) with 25.5% residue, which is associated with the presence of cross-linked structure that does not decompose at the maximum heating temperature. In other samples, CI particles were added to the silicone rubber matrix from (10%–40%) volume fraction of CIPs. As it is obvious, by increasing the amount of magnetic particles weight losing decreases, which is due to the good interaction between polymeric matrix and CIPs. In addition, the DTG curves depicted in Fig. 13.16 which shows the maximum decomposition rate temperature, T_p , the difference between T_p of bare sample and E-40% is around 20°C which is related to the lower fraction of cross-linked structure before decomposition. By decreasing the fraction of cross-linked structure it can be concluded that the most interaction among the surface of the CIPs and silicone rubber matrix had been occurred (Perales-Martínez et al., 2017).

In another study on the temperature stability of MRFs and CIP particles coated by polymeric materials, research by Jiang et al. (2010) has been considered. The CI particles have been coated by PMMA with emulsion polymerization approach. Fig. 13.17 shows the TGA curves of PMMA and CI and CI-PMMA particles. The loss weight in Fig. 13.17A indicates the degradation of the polymeric layer on the CI particles which is around 250–400°C. Fig. 13.17B depicts the weight changes of both CI and CI-PMMA composite. For the CI curve, there is an increase in weight which is due to oxidation of CI particles but for the CI-PMMA curve at the first there is a slight decrease in the range of 200–400°C which is attributed to degradation of polymeric layer and the next increase is relevant to oxidation of CI particles.

Isobutylene-isoprene rubber (IIR) as a polymeric matrix has been widely used due to its thermal and oxidative stability, chemical resistance and high damping properties. Wang et al. (2006) had been characterized the thermal stability of IIR by using TGA analyses. Fig. 13.18 shows the TG curves of pure iron, IIR with

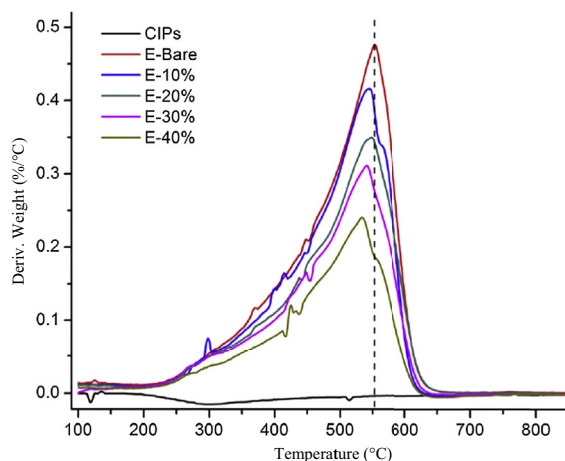
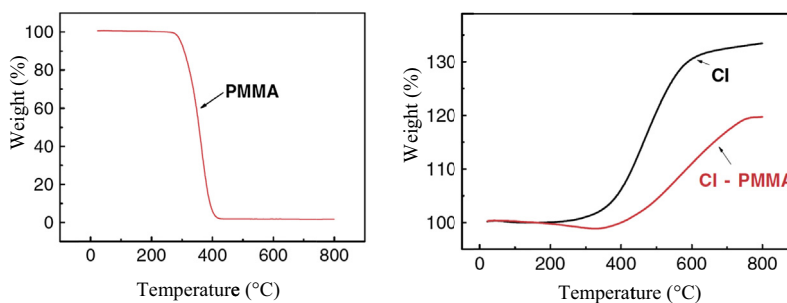
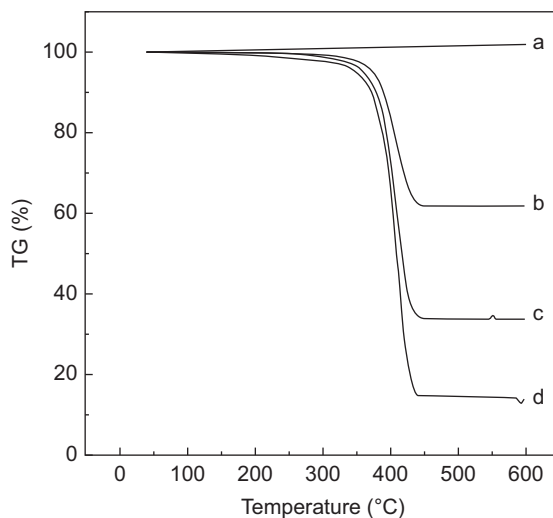


FIGURE 13.16

DTG curves of the MRE samples (Perales-Martínez et al., 2017).

**FIGURE 13.17**

TGA curves of (A) PMMA and (B) CI and CI-PMMA particles (Jiang et al., 2010).

**FIGURE 13.18**

TG analysis of (a) pure Fe (b) MR elastomers with 15% vol Fe (c) MR elastomers with 5% vol Fe (d) IIR filled with 5% vol CB (Wang et al., 2006).

15% vol Fe, IIR with 5% vol Fe and IIR filled with 5% vol CB (carbon black). As it obvious from the figure, the mass of pure Fe remained constant and the most loss in the mass is relevant to IIR with CB. While adding the CI to the IIR matrix improves the thermal stability of IIR matrix in comparison with adding CB.

5.4 Damping and elastic behavior

The total damping ratio of MR polymer materials composited with magnetic particles comes from each component. In addition, if the components combine together weakly, there will be some energy dissipation on the intersection. Therefore, the

total damping ratio will be consisting of any components and the energy dissipation on the intersection. The MR polymer as a weak intersection composite can be expressed as (Eq. 13.7):

$$D = \phi_m D_m + \phi_p D_p + D_s \quad (13.7)$$

where ϕ_m and ϕ_p are the percentage in volume of the matrix and the particle, respectively. D_m and D_p are the damping ratio of the matrix and the particle, respectively, and D_s denotes the energy dissipation coming from the intersection between the inner particles and the matrix in unit volume.

The damping ratio of the particle D_p is more less as compared to that of polymer matrix, the above equation can be modified into:

$$D = \phi_m D_m + D_s \quad (13.8)$$

Here D_s can be described as:

$$D_s = nfS \quad (13.9)$$

where n is the number of particles in the unit volume of MR elastomers, f is the sliding frictional force between the particle and matrix, and S is the displacement of interfacial slipping.

By applying the external field, a magnetic force will be applying to the particles and will transfer from the particles to the polymeric matrix. The polymeric matrix is a kind of soft material which easily transforms by the presence of external force. So, in the meantime the average friction force comes up:

$$F = \mu(F_0 + F_m) \quad (13.10)$$

where μ is the friction factor between the iron particle and the matrix, and F_0 and F_m is interaction between particle and matrix without and with a magnetic field, respectively. Thus, the damping ratio of elastomers can be expressed as follows (Chen and Gong, 2008):

$$D = \phi_m D_m + \mu n(F_0 + F_m)S \quad (13.11)$$

Yang et al. (2012) have been investigated the damping behavior of magnetorheological elastomers. In this research, the overall damping has been found to be directly related to the CIP content and strain amplitude. The obtained results are demonstrating in Table 13.3.

Damping of MR polymer materials composed of three-type damping: the intrinsic damping, the interface damping and the magnetomechanical hysteresis damping. In low contents of CIPs and strain amplitude, intrinsic damping plays a dominant role. However, the interface damping is predominant at higher strain amplitude or higher CIP contents. Based on the given table, it is evident that by increasing the strain amplitude and CIPs, the interface damping overcomes other damping categories.

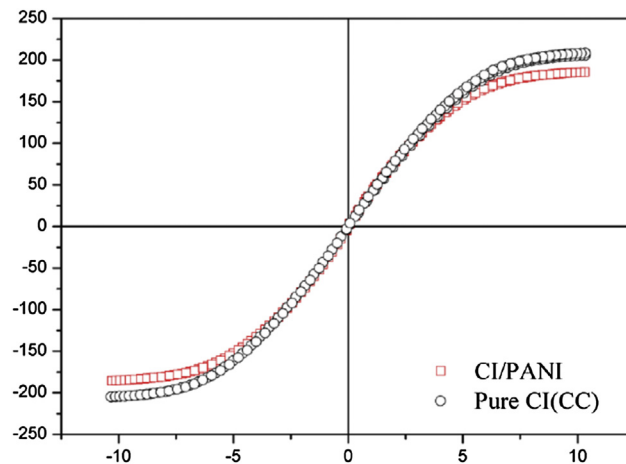
Table 13.3 The damping capacities of different samples under different magnetic intensities (Yang et al., 2012).

Sample	Magnetic intensity				
	0	0.2T	0.4T	0.6T	0.8T
MRE-40	0.1288	0.1307	0.1309	0.1307	0.1305
MRE-50	0.1459	0.1440	0.1443	0.1436	0.1418
MRE-60	0.1649	0.1710	0.1722	0.1722	0.1722
MRE-70	0.2080	0.2028	0.2024	0.2016	0.2005
MRE-80	0.2391	0.2408	0.2410	0.2411	0.2408

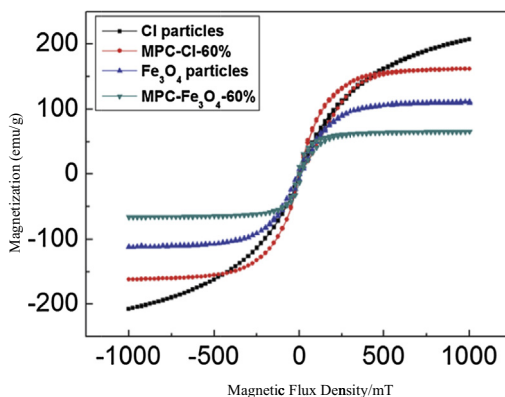
5.5 Magnetic properties of MR polymers

Composite materials with different contents of magnetic particles show different magnetic properties. The saturation magnetization (B_s) value in the MR polymer as the composite material differs by changing the content of iron nanoparticles; increases by increasing the iron nanoparticle. On the other hand, the B_s value of composite is lower than that of pure iron nanoparticles. It can be due to the fact that the content of iron, and the other reason can be the polymer matrix shields, the external magnetic field and prevents the particles to response to it, also the morphological defects can reduce the response ability (Tan et al., 2010).

Fig. 13.19 shows the magnetic properties of both pure CI particles and CI/PANI which had investigated by Moon et al. (2016). As it is obvious from the figure, the saturation magnetization of the pure CI differed from that of CI/PANI particles; decreasing from 204 (pure CI) to 185 (CI/PANI) emu/g. and the density of the CI/PANI was decreased to 7.05 g/cm³ from 7.86 g/cm³ for pure CI. These decrease

**FIGURE 13.19**

VSM curve of pure CI (CC) particles and CI/PANI microspheres (Moon et al., 2016).

**FIGURE 13.20**

Hemagnetic hysteresis loops of MPC—Fe₃O₄-60%, MPC—CI-60% and CI particles (Wang et al., 2014).

for both saturation magnetization and density can be due to coating the PANI on the magnetic particles.

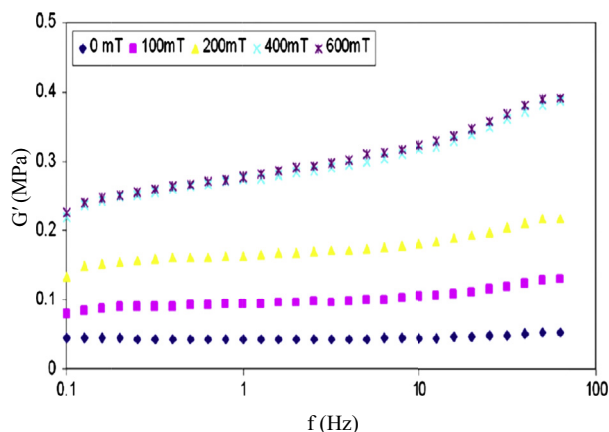
To evaluate the magnetic property of another polymeric material, Wang et al.'s (2014) investigation had been considered. Fig. 13.20 indicates hysteresis loop of MPC (multi-functional polymeric composite)-Fe₃O₄ 60%, MPC-CI-60% and CI particles. As it is obvious, all the samples show soft magnetic behavior. The saturated magnetization of MPC- Fe₃O₄ 60%, MPC-CI-60% and CI particles and Fe₃O₄ particles were 59.5, 160.7, 207.2 and 111.3 emu/g, respectively. By comparing the data, it can be found that CI particles have more positive effect on saturation of polymeric matrixes rather than Fe₃O₄ particles.

5.6 Rheological property

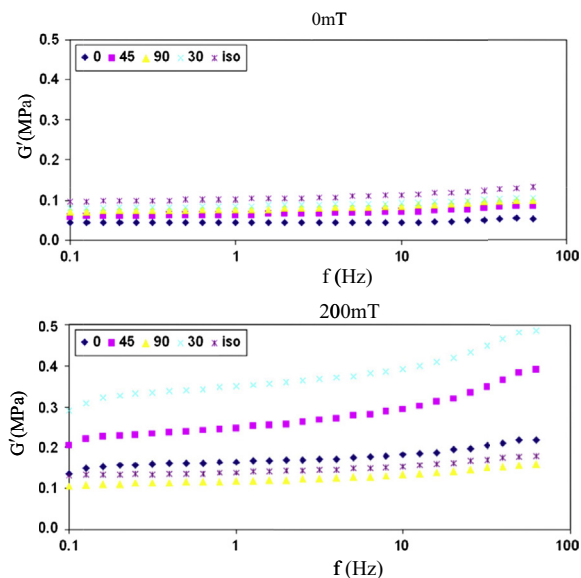
In viscoelastic materials, and as indications of the magnetorheological effect, there are two kinds of modulus. The first storage modulus (G') is known as the ability of viscoelastic material to store the energy of deformation, and the second; loss modulus (G'') represents the ability of material to dissipate the energy of deformation as heat.

Fig. 13.21 shows the changes of storage modulus at different magnetic field strength. In this investigation which had done by Anna Boczkowska et al. (2012), the chosen matrix is soft polyurethane. As it is obvious from the figure, storage modulus increases by increasing the magnetic field. Fig. 13.22 indicates the changes in storage modulus with different particles arrangement within the matrix. The particles align in perpendicular (90 degrees) to the magnetic field, which cause the lowest change in G' . From the other hand, the highest increases in storage modulus are attributed to that with particle chains deflected at 45 and 30 degrees.

In another study by Böse and Röder (2009) using of silicone consisted of polydimethylsiloxane as the matrix material with two different kinds of small (5 μm) and

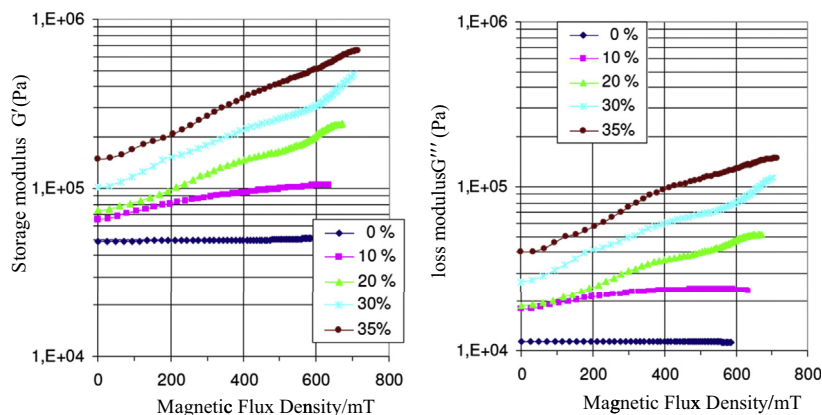
**FIGURE 13.21**

Storage modulus G_0 versus angular frequency f for different magnetic field strengths — Fluka carbonyl-iron with 0 degree alignment of the particles (Boczkowska et al., 2012).

**FIGURE 13.22**

Storage modulus G_0 versus angular frequency f for 0 and 200 mT magnetic field strengths — Fluka carbonyl-iron with different alignment of particles (Boczkowska et al., 2012).

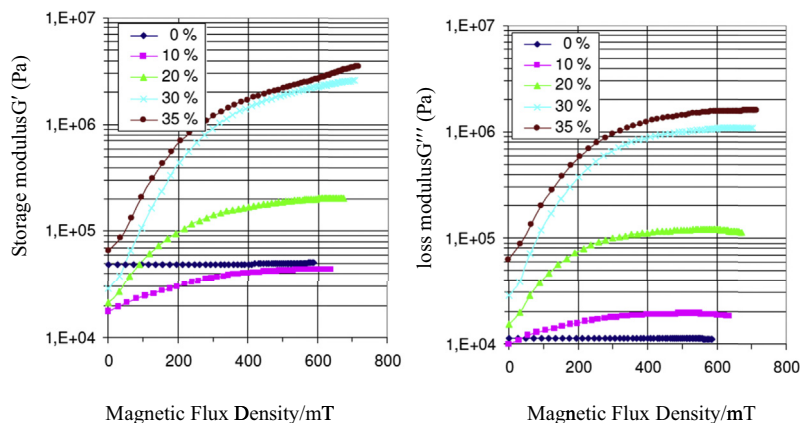
large ($40\text{ }\mu\text{m}$) particles, and the effect of magnetic field strength and frequency on storage modulus and loss modulus has been investigated. Fig. 13.23 shows the changes of storage modulus and loss modulus with various contents of small iron particles by increasing the magnetic field intensity. As it is clear from the figure,

**FIGURE 13.23**

Dependence of storage modulus (left) and loss modulus (right) of isotropic MRE with different concentrations of small iron particles (in vol.%) in silicone on the magnetic flux density (Böse and Röder, 2009).

by increasing the small iron particles concentration and magnetic flux intensity both storage and loss modulus increases. And also it is obvious that in all conditions the elastic properties overcome to the viscous behavior of the composites.

MRE samples with large iron particles with isotropic arrangements are depicted in Fig. 13.24. The absolute increase in both storage and loss modulus by increasing the magnetic flux intensity has been achieved and also drastically higher than for samples with small iron particles.

**FIGURE 13.24**

Dependence of storage modulus (left) and loss modulus (right) of isotropic MRE with different concentrations of large iron particles (in vol.%) in silicone on the magnetic flux density (Böse and Röder, 2009).

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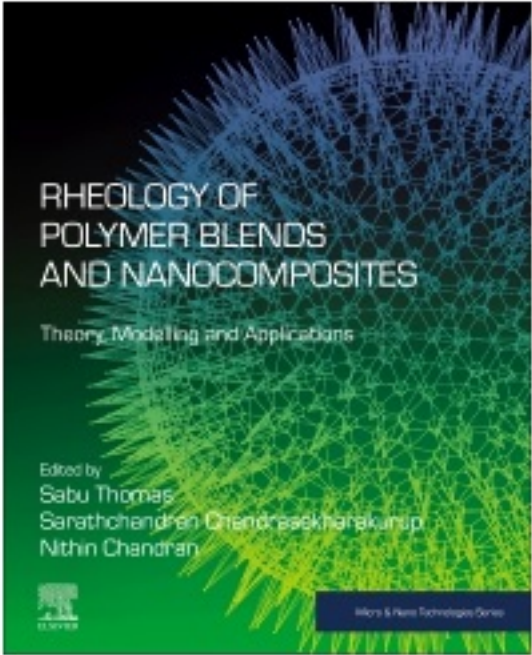
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RHEOLOGY OF POLYMER BLENDS AND NANOCOMPOSITES

Theory, Modelling and Applications

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