1

Polymer Blends: State of the Art, New Challenges, and Opportunities

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1.1

Introduction

A polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical properties. Generally, there are five main types of polymer blend: thermoplastic–thermoplastic blends; thermoplastic–rubber blends; thermoplastic–thermosetting blends; rubber–thermosetting blends; and polymer–filler blends, all of which have been extensively studied. Polymer blending has attracted much attention as an easy and cost-effective method of developing polymeric materials that have versatility for commercial applications. In other words, the properties of the blends can be manipulated according to their end use by correct selection of the component polymers [1]. Today, the market pressure is so high that producers of plastics need to provide better and more economic materials with superior combinations of properties as a replacement for the traditional metals and polymers. Although, plastic raw materials are more costly than metals in terms of weight, they are more economical in terms of the product cost. Moreover, polymers are corrosion-resistant, possess a light weight with good toughness (which is important for good fuel economy in automobiles and aerospace applications), and are used for creating a wide range of goods that include household plastic products, automotive interior and exterior components, biomedical devices, and aerospace applications [2].

The development and commercialization of new polymer usually requires many years and is also extremely costly. However, by employing a polymer blending process – which is also very cheap to operate – it is often possible to reduce the time to commercialization to perhaps two to three years [2]. As part of the replacement of traditional polymers, the production of polymer blends represents half of all plastics produced in 2010. Today, the polymer industry is becoming increasingly sophisticated, with ultra-high-performance injection molding machines and extruders available that allow phase-separations and viscosity changes to be effectively detected or manipulated during the processing stages [3]. Whilst this modern blending technology can also greatly extend the performance capabilities of

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polymer blends, increasing market pressure now determines that, for specific applications, polymer blends must perform under some specific conditions (e.g., mechanical, chemical, thermal, electrical). This presents a major challenge as the materials must often function at the limit of the properties that can be achieved; consequently, in-depth studies of the properties and performance of polymer blends are essential.

1.2
Miscible and Immiscible Polymer Blends

Generally, polymer blends are classified into either homogeneous (miscible on a molecular level) or heterogeneous (immiscible) blends. For example, poly(styrene) (PS)–poly(phenylene oxide) (PPO) and poly(styrene-acrylonitrile) (SAN)–poly (methyl methacrylate) (PMMA) are miscible blends, while poly(propylene) (PP)–PS and poly(propylene)–poly(ethylene) (PE) are immiscible blends. Miscible (single-phase) blends are usually optically transparent and are homogeneous to the polymer segmental level. Single-phase blends also undergo phase separation that is usually brought about by variations in temperature, pressure, or in the composition of the mixture.

Since, ultimately, the properties of a polymer blend will depend on the final morphology, various research groups have recently undertaken extensive studies of the miscibility and phase behavior of polymer blends. In practice, the physical properties of interest are found either by miscible pairs or by a heterogeneous system, depending on the type of application. Generally, polymer blends can be completely miscible, partially miscible or immiscible, depending on the value of ΔG_m [4].

The free energy of mixing is given by

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1.1}$$

For miscibility (binary blend), the following two conditions must be satisfied: the first condition $\Delta G_m < 0$; and the second condition

$$\left(\frac{\partial^2(\Delta G_m)}{\partial \phi_i^2}\right)_{T,p} > 0 \tag{1.2}$$

where ΔG_m is the Gibbs energy of mixing, ϕ is the composition, where ϕ is usually taken as the volume fraction of one of the components.

ΔS_m is the entropy factor and is a measure of disorder or randomness, is always positive and, therefore, is favorable for mixing or miscibility especially for low-molecular-weight solutions. In contrast, polymer solutions have monomers with a high molecular weight and hence the enthalpy of mixing (ΔH_m) is also a deciding factor for miscibility. ΔH_m is the heat that is either consumed (endothermic) or generated (exothermic) during mixing. If the mixing is exothermic then the system is driven towards miscibility. The mixing is exothermic only when strong specific interactions occur between the blend components. The most common specific interactions found in polymer blends are hydrogen bonding, dipole–dipole, and ionic interactions. Several techniques that can be used to understand the specific interaction in polymers, such as Fourier transform infrared (FTIR) spectroscopy, small-angle neutron scattering, ellipsometry, neutron reflectivity, and nuclear magnetic resonance (NMR) spectroscopy.

Experimentally observed phase diagrams in polymer blend systems may be lower critical solution temperature (LCST), upper critical solution temperature (UCST), combined UCST and LCST, hourglass-, and/or closed-loop-shaped. The most commonly observed phase diagrams are LCST (phase separation of a miscible blend during heating) and UCST (phase separation of a miscible blend during cooling). Phase separation in polymer solutions may proceed either by nucleation and growth (NG) or by spinodal decomposition (SD), or by the combination of both [5]. Experimentally, phase separation can be followed by a number of experimental techniques that include light scattering, neutron scattering, ellipsometry, and rheology. The generated morphology can be characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM) fluorescence microscopy, infrared, near-infrared and Raman imaging, and confocal microscopy.

1.3
Compatibility in Polymer Blends

In general, the compatibility between the polymer phases decides the properties of a heterogeneous polymer blend [6,7]. The interface between the polymer phases in a polymer system is characterized by the interfacial tension which, when approaching zero, causes the blend to become miscible. In other words, if there are strong interactions between the phases then the polymer blend will be miscible in nature. Large interfacial tensions lead to phase separation, with the phase-separated particles perhaps undergoing coalescence; this will result in an increased particle size and, in turn, decreased mechanical properties. The interfacial tension can be reduced by the addition of interfacial agents known as compatabilizers [8]; these are generally molecules with hydrophobic and hydrophilic regions that can be aligned along the interfaces between the two polymer phases, causing the interfacial tension to be reduced and the compatibility of the polymer blends to be increased. Compatibility results in a reduction of the dispersed particle size, an enhanced phase stability, and increased mechanical properties [8]. The physical properties of miscible, compatabilized and uncompatabilized blends can be characterized using techniques such as thermogravimetric analysis, dynamic mechanical thermal analysis, and universal testing machines.

1.4
Topics Covered in this Book

The following chapters in this book provide a comprehensive overview on the miscibility, phase separation, morphology and other fundamental properties of polymer blends, using a wide range of state-of-the-art techniques. For example, Chapter 2 relates to the miscibility of polymer blends, and provides an overview of the theory behind the phase separation of polymer blends, with specific examples. Chapter 3 describes the compatibility of polymer blends and discusses the influence of compatabilizers on phase morphology and structural properties. Chapter 4 provides a comprehensive review of the rheological properties of thermosetting blends and composites, while Chapter 5 provides details of the light scattering of polymer blends and outlines the theory and applications of light-scattering techniques for studying the phase behavior of polymer blends. In Chapter 6, a survey is provided of the characterization of polymer blends, using X-ray scattering techniques, while Chapter 7 details the basis for using neutron scattering when studying the phase behavior of polymer blends and block copolymer systems. In Chapter 8, the applications of ultrasound on polymer blends are reviewed; these include the characterization of polymer blends, polymer modification, property enhancement and the monitoring of polymer processing. The theories and applications of ellipsometry on polymer blends are discussed in Chapter 9, applications include phase separation, morphology, nanoporosity, adhesive and adsorption properties. Chapter 10 discusses the theories and applications of inverse gas chromatography on polymer blend systems; the advantages and drawbacks of inverse gas chromatography are also discussed in detail. In Chapter 11, the thermal stability of polymer blends is discussed, outlining the changes in thermal stability by blending, together with some specific examples. The application of dynamic mechanical thermal analysis (DMTA) for the study of polymer blends is described in Chapter 12, together with details of the theoretical bases underlying viscoelastic theory, the study of segmental dynamics, free volume and dynamic fragility, and the study of miscibility or the effect of adding plasticizers and chemical or physical crosslinkers. An overview of the thermomechanical properties of polymer blends is provided in Chapter 13, where the importance of particle size on polymer toughening is stressed. Chapter 14 provides a comprehensive review on water sorption and solvent sorption behavior that can be expected from miscible or immiscible but compatible polymer blends. The authors of this chapter concluded that miscibility depends on the molecular structures of the both polymers, morphologies and blend composition, as well as the processes of the blends. Numerical simulation models and methods for polymer blends are covered in Chapter 15, while Chapter 16 deals with the latest microscopic techniques that have the capability to observe the three-dimensional structural details in polymer blend films. In Chapter 17, the morphologies of different types of polymer blends investigated by various microscopic techniques are discussed, with special reference to sample preparation and comparison among SEM, TEM and AFM. In Chapter 18, the most sensitive surface technique, namely secondary ion mass spectrometry (SIMS), is described, which allows molecular and highly spatially resolved lateral information to be obtained. In Chapter 19, the authors discuss the morphology of different types of polymer blends, using fluorescence microscopy to determine the quantitative spatial distribution and molecular information of the polymer components. In Chapter 20, the potential of FTIR techniques for determining the properties of polymers blends both quantitatively and qualitatively is highlighted, while in Chapter 21 hydrogen-bonding interactions between the polymer components, determined using NMR spectroscopy, are discussed. Chapter 22 provides details of the phase morphology of polymer blends using infrared, near-infrared and Raman imaging, while in Chapter 23 the application of, and recent advances in, the characterization of polymer blends using electron spin resonance (ESR) spectroscopy and forward recoil spectroscopy, are discussed. In Chapter 24, attention is focused on the optical properties of polymer blends, in both ultraviolet and visible ranges of light, to investigate the miscibility of polymer blends, while Chapter 25 focuses on the driving forces that produce miscibility in polymer blends, using fluorescence spectroscopy. Chapter 26 provides a comprehensive overview of recent developments and progress in the molecular dynamics, miscibility, nature of interaction, crystallization behavior, and curing kinetics of representative examples of polymer blends using dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization current (TSDC) techniques. Finally, in Chapter 27 attention is focused on the miscibility of polymer blends, using positron annihilation spectroscopy.

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