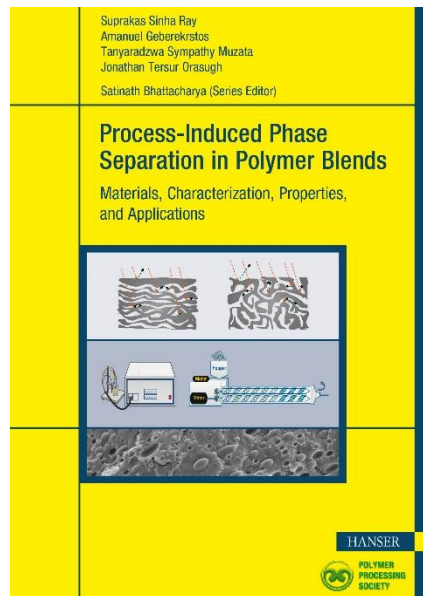


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## Sample Pages

# Process-Induced Phase Separation in Polymer Blends

Suprakas Sinha Ray, Amanuel Geberekrstos, Jonathan Tersur Orasugh and Tanyaradzwa Sympathy Muzata

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tions in energy storage and EMI shielding.

# Preface

Phase separation in polymer blends has attracted tremendous techno-commercial importance from fundamental to practical applications. Most applications of polymer blends, such as tissue engineering, membrane technology, electromagnetic shielding, energy harvesting, structural materials, packaging, smart multiphase polymer coatings, and others, depend on the morphologies developed during processing. Conventionally, phase-separated polymer blends can be prepared and their properties tuned via various processing techniques. However, in some cases, their processing methods using predetermined conventional polymer processing techniques require modifications before usage. The dynamic properties of these polymers are strongly linked with stress–diffusion coupling and viscoelastic effects. It is, in theory, possible to examine the nucleation-limited mechanism of phase separation in polymer blends; nevertheless, experimentally, it is more challenging. Diverse phase-separated polymeric structures can be prepared depending on the thermodynamic aspects of the polymer pairs, where it is important to understand the basics of the phase separations in these polymer blends within the context of the miscibility of these polymers. In the research and/or review literature reported to date it is shown that several properties such as morphologies, response to external stimuli, and mechanical properties of phase-separated polymers as per intended application can be created by simply altering the dynamic and kinetic parameters such as the viscosity ratio, blend ratio, mixing time, compatibilization, and mixer sort.

Currently, there is no dedicated authored book on this topic; the few review articles and reports either concentrate on specific phase-separated polymer blends and perspectives or deliver only short descriptions with limited instances. Thus, there is a need for a comprehensive, authored book presenting an exhaustive and serious overview of state of the art in phase-separated or multiphase polymer blends, including significant past and recent developments. Moreover, there is a need to address fundamental issues that persist regarding phase-separated polymer blends and their nanocomposites, which could profile future research and industrial application of these materials for a novel sustainable future development. This book emphasizes recent research developments, processing techniques, char-

acterization methods, factors influencing phase separation temperature in phase-separated, including partially miscible, polymer blends, and key research challenges in developing phase-separated polymer materials as per literature in different application areas.

The field of polymer blends has rapidly grown over the past years, as witnessed by the number of publications being produced yearly. Since polymer blends are a vast area, it is of paramount importance to fully exploit it from a fundamental aspect to applying the multiphasic polymeric material. The journey from fundamentals to the application of polymer blends is one area that is still lacking, and this book is systematically structured to cater to this need. This book will extensively cover the thermodynamics of polymer blends and the fabrication of multiphasic polymeric systems with a precise and unique architecture.

This book will be most valuable to the reader as it will extensively outline (i) the fundamental aspect of polymer blend thermodynamics, (ii) the state-of-the-art processing techniques for specific polymer blend systems currently in use, and (iii) the design and fabrication of multiphasic polymeric materials, which will present a multiplicity of opportunities in water remediation, packaging and electronic industries to mention a few.

The first chapter provides an overview of polymer blend technology. Chapter 2 focuses on phase separation, heterogeneous behavior, and prevention of phase separation in immiscible polymer blend systems. Crystallization and melting kinetics of phase-separated polymer blends are reported in the Chapter 3. The fourth chapter introduces and explains various theoretical studies of polymer blends. The fifth chapter summarizes different processing techniques used to prepare polymer blends. Experimental approaches for the evaluation of the phase separation process in polymer blends are reported in Chapter 6. Chapter 7 focuses on factors influencing phase separation in partially miscible polymer blends. Chapter 8 reports interfacial modification of immiscible polymer blends. Finally, Chapter 9 summarizes various industrial applications of polymer blends.

This book is ideal for polymer scientists and engineers, material scientists, researchers, and engineers, including under- and post-graduate students who are interested in this exciting field of research. It will also help industrial researchers and R&D managers who want to bring advanced phase-separated polymer materials/products into the market.

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# 1

## Introduction

### ■ 1.1 Overview of the Polymer Blend Technology

Multiphase polymer blend systems have resulted in the advent of new technologies, which are of great significance in their different applications. The combination of two different polymers has led to the tailoring of multiphase systems possessing optimized characteristics. The blending of two polymers leads to either miscible polymer blend systems like poly(methyl methacrylate) (PMMA)/styrene-acrylonitrile copolymer (SAN) [1–3], polystyrene (PS)/poly(vinyl methyl ether) (PVME) [4, 5], and poly(methyl methacrylate) (PMMA)/poly(styrene-co-maleic anhydride) (SMA) [6] or immiscible polymer blend systems such as polycarbonate (PC)/poly(vinylidene fluoride) (PVDF) [7] and PS/PMMA [8]. This aspect will be further explained in the following chapters. Miscible polymer blend systems are a class of blends that can be fundamentally investigated to understand their equilibrium and non-equilibrium properties fully and how the demixing temperature can be altered in the presence of nanomaterials, for example, graphene oxide (GO) [9], graphene, carbon nanotubes (CNTs), and silica to mention a few. The miscibility of polymer blend systems is determined by an interaction parameter which is commonly known as the Flory–Huggins interaction parameter. The interaction parameter is mainly dependent on temperature and composition. It is important to fully understand the fundamentals behind phase separation because the resultant morphologies determine the specific application of the polymer blend system.

#### 1.1.1 Demixing in Polymer Blend Systems

Several publications, patents, and theses about polymer blends fundamentally show their importance in different applications [10–12]. The advent of polymer blend systems, whether miscible or immiscible, resulted from the plethora of ad-

vantages they offer. Polymer blends result in multiphasic materials that have the required properties for a specific application at a low cost. It is relatively inexpensive to blend two polymers than to go into the laboratory and start synthesizing a new class of polymer with specific desired properties. Polymer blends also improve the recycling of petroleum-based polymers; it is well known that polymers have become a menace to the environment resulting in different types of pollution. This can be curbed by blending petroleum-based polymers with biodegradable polymers. Several polymers have a high glass transition temperature ( $T_g$ ), resulting in them being very strenuous to process due to the elevated temperatures needed for them to flow. To ensure the effective processability of such polymers, they can be blended with polymers that have low  $T_g$ . The addition of nanomaterials into polymer blends has been a game changer because these nanomaterials induce significant effects on the properties of the polymer blends, whether immiscible or miscible. In immiscible polymer blend systems, nanomaterials can act as compatibilizers, increasing the interfacial adhesion of the two polymers; this will be further explored in **Chapter 8**. The incorporation of nanomaterials can lead to a decrease or increase in the demixing/phase separation temperature of miscible polymer blends. They can also affect the segmental motion of the polymer chains, causing either an increase or decrease in  $T_g$  and the crystallization temperature ( $T_c$ ).

## ■ 1.2 Different Types of Miscible Polymer Blend Systems

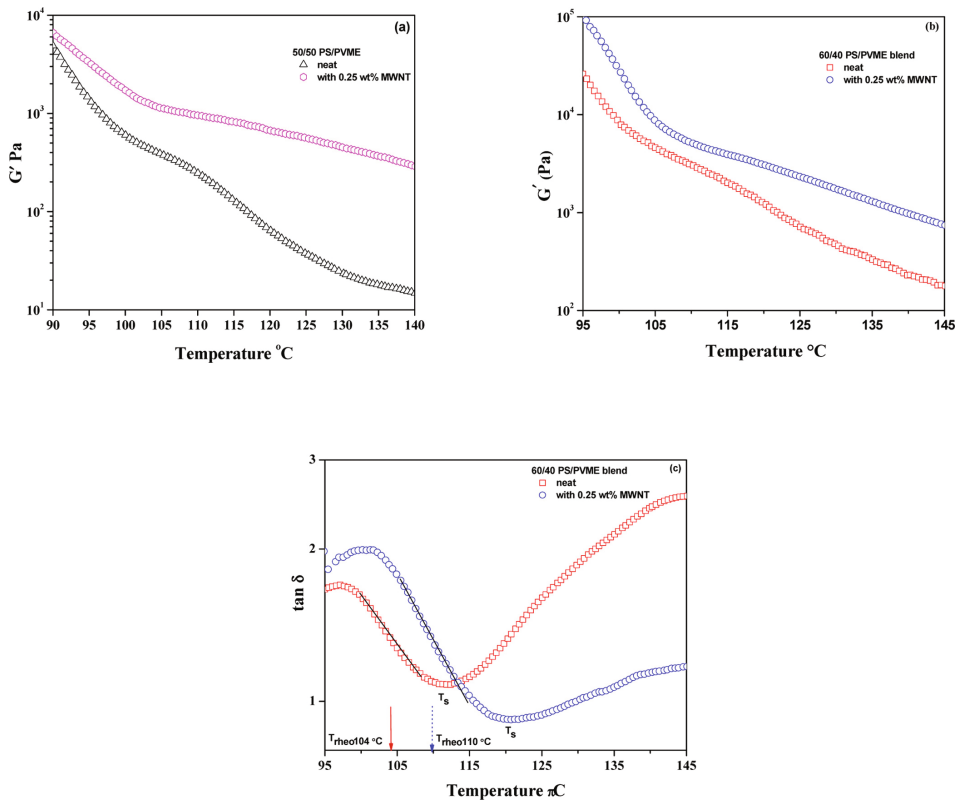
### 1.2.1 PMMA/SAN Blend Systems

PMMA/SAN is an example of a miscible polymer blend system. This polymer blend system phase separates at high temperatures and is miscible at low temperatures [13]. The miscibility of this system is a result of the copolymer repulsion effect between the acrylonitrile and phenyl units. PMMA/SAN can be prepared by solution mixing or melt mixing method. Preparation by melt mixing is the most ideal because it is the type of method which is currently being used in industry [14]. The solution mixing method is less favored because it makes use of large amounts of solvents that have detrimental effects on human health and the environment. It should also be highlighted that the number of samples that can be prepared by solution mixing is lower, and the time taken to evaporate the solvent is very long, usually requiring at least four days. Different types of nanoparticles have been reported to induce changes in polymer systems [15]. The incorporation

of nanomaterials into PMMA/SAN was reported to increase the demixing temperature of the polymer blend system. Graphene oxide nanosheets, both neat and functionalized forms, were reported to increase the demixing temperature of PMMA/SAN [1, 9]. It was also reported that the addition of silica nanoparticles enhanced the demixing temperature in PMMA/SAN blend [3]. The increase in the demixing temperature was caused by the interaction of the PMMA chains with the nanoparticles; this interaction decreases the PMMA molecular weight in the bulk phase. Pang and co-workers [2] also studied the effect of nanoclay on the demixing temperature of PMMA/SAN. They observed an increase in both the binodal and the spinodal demixing temperatures after incorporating nanoclay particles in the blend systems.

### 1.2.2 PS/PVME Blend Systems

PS/PVME is a dynamic asymmetrical polymer blend system [16]. The  $T_g$  of PS and PVME are far apart from each other, resulting in a demixing temperature that can be observed by melt rheology. PS/PVME is another example of a low critical solution temperature (LCST) polymer blend system, as it is miscible at low temperatures but demixes at high temperatures [17]. The incorporation of different types of nanomaterials, whether functionalized or nonfunctionalized nanoparticles, was found to affect the demixing temperature of the PS/PVME blend. The addition of multi-walled CNTs (MWCNTs) was found to increase the demixing temperature of near-critical compositions. A study by Xavier et al. [5] showed that 0.25 and 0.5 wt.% of CNT increased the demixing temperature of PS/PVME as revealed by melt rheology and dielectric spectroscopy. The nanoparticle effect in the 50/50 and 60/40 blend compositions can be seen in Figure 1.1. Melt rheology is one of the widely used techniques investigating how the nanoparticles affect the demixing temperature of miscible polymer blends [6]. Other characterization techniques like optical and electron microscopes can be affected by turbidity or the presence of nanoparticles, but rheology is not affected.



**Figure 1.1** Isochronal dynamic temperature ramp performed at  $\omega = 0.1$  rad/s, 1% strain with a  $0.5^\circ\text{C}/\text{min}$  heating rate for 50/50 PS/PVME blends with and without multiwalled carbon nanotubes (MWNTs) (0.25 wt.%): (a)  $G'$  versus temperature; and for 60/40 PS/PVME blends with and without MWNTs (0.25 wt.%), (b)  $G'$  versus temperature, (c)  $\tan \delta$  versus temperature. Reprinted with permission from [5]. Copyright 2013, American Chemical Society

Reduced GO (rGO) was also found to affect the demixing temperature of PS/PVME [18]. The incorporation of rGO increased the demixing temperature of PS/PVME. Kar and co-workers [19] went a step further in fabricating polymer-grafted nanoparticles. PS polymer chains were grafted onto the surface of silver nanoparticles and incorporated into PS/PVME polymer blend. PS polymer, which was blended with PVME, was bromo-terminated. The polymer grafted silver nanoparticles were found to increase the spinodal demixing temperature of the polymer blend system. The incorporation of spherical nanoparticles, which have a radius comparable to the radius of gyration of the polymer chains, can result in an increase in the demixing temperature. When polymer chains cover the spherical nanoparticles, there is a reduction in interaction between the two polymers (PS/PVME), increasing the demixing temperature of the polymer blend [20].

### 1.2.3 PVDF/PMMA Blend Systems

PVDF/PMMA is another example of a miscible polymer blend system in the melt state. The miscibility of this system is mainly a result of the dipole-dipole interaction between the  $\text{CF}_2$  and  $\text{CH}_2$  of PVDF and PMMA, respectively, and also due to the formation of hydrogen bonding between the  $\text{CH}_2$  found in PVDF and the PMMA carbonyl group [21]. The PVDF/PMMA polymer system shows both LCST and upper critical solution temperature (UCST) characteristics. As explained earlier, the polymer blend is miscible at high temperatures in its melt state and demixes at low temperatures due to crystalline-induced phase separation.

## ■ 1.3 Immiscible Polymer Blend Systems

### 1.3.1 Polypropylene (PP)-Based Blend Systems

PP is one of the most used polyolefins in the world due to its low cost and availability. PP can be used to make polymer blend systems that can be used in several applications. PP can exist in three different forms atactic, syndiotactic, and isotactic. PP is widely blended with other polymers because of its outstanding thermal, mechanical, and chemical properties resulting in it being used in a number of applications, for example, automotive, medical, and packaging. An immiscible polymer blend system can be produced when PP is blended with a polar polymer, and this may usually result in poor mechanical properties. In order to improve the interfacial adhesion of PP and other polar polymers, compatibilizers can be used. The different types of compatibilizers will be extensively explored in **Chapters 7 and 8**. Polylactic acid (PLA) can be used in packaging and biomedical applications because it is a biocompatible and biodegradable polymer. Despite its ability to degrade, this polymer has several limitations, such as poor mechanical properties. These shortfalls can be prevented by blending PLA with PP to establish a PLA/PP polymer blend. The overall properties of the blend can be tailored by tuning the composition of one of the polymers, the addition of compatibilizers or nanoparticles, and the method of processing. The addition of nanoclay into the PLA/PP polymer blend system can enhance both the mechanical and thermal properties of the system resulting in the system being used in applications that require high mechanical properties and elevated temperatures [22]. Two polyolefins can also be blended with the help of a compatibilizer to improve their interfacial adhesion. Blending two polymers has resulted in tailoring multiphasic systems with high thermal conductivity. Polymers have been well known to have low thermal con-

ductivity, and this can be improved by incorporating nanoparticles that can be localized on the interface of the immiscible blend system. Jing et al. [23] blended polyethylene (PE) and PP and incorporated hexagonal boron nitride (h-BN), which was wrapped with styrene-ethylene-propylene-styrene (SEPS) [23]. An improvement in the thermal conductivity of the blend system was observed. This can allow this system to be applied in different applications that require elevated thermal conductivity and poor electrical properties. PP can also be blended with poly( $\epsilon$ -caprolactone) (PCL) to improve its degradability. PP can be oxidized to improve its compatibility with PCL. In a study conducted by Arcana and co-workers [24], oxidized PP was blended with PCL via the solution casting method. The degradability of the polymer blend system was shown to improve as the PCL content was increased.

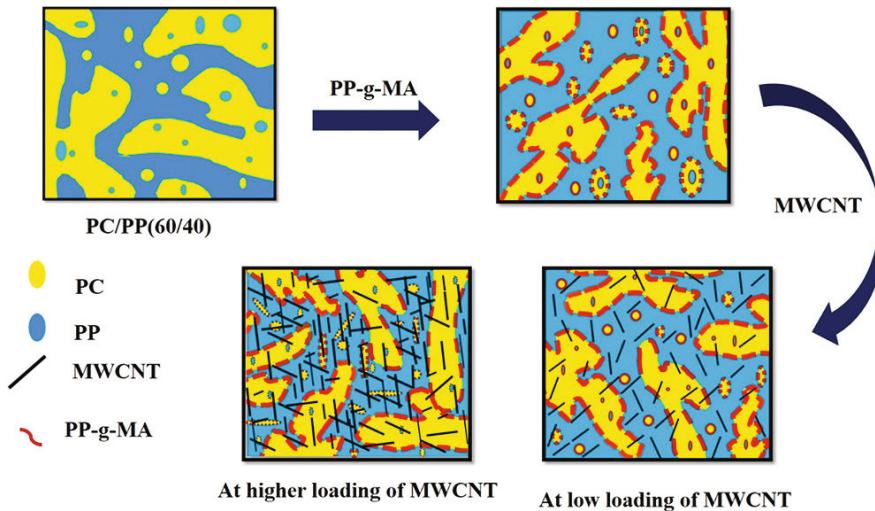
### 1.3.2 PE-Based Polymer Blend Systems

PE is a polymer that causes different types of pollution when dumped in the environment. In an endeavor to improve its environmental impact through fast degradation, PE has been blended with different types of biodegradable polymers. Starch, a natural polymer derived from different plants, is one of the biobased biodegradable polymers that has been recently blended with PE to reduce its environmental impact. Low-density PE (LDPE) and starch were blended, and it was observed that increasing the amount of starch in the blend system improved its degradability [25]. In another study, PE was blended with different biodegradable natural polymers, including starch, dextrin, modified wood flour, nonmodified wood flour, and lignin [26]. The main aim of the study was to investigate to what extent LDPE degrades in the presence of the above-mentioned natural polymers. It was shown an increase in the content of the natural polymers influences the degradation of LDPE.

### 1.3.3 PC-Based Polymer Blend Systems

PC is an engineering amorphous and transparent polymer that can be mixed with other polymers, thus taking advantage of its properties to produce polymer blend systems that can be used in different applications such as electromagnetic interference (EMI) shielding. When PC is blended with a commodity plastic such as PP, it mostly produces an immiscible polymer blend, and the interfacial adhesion can be improved by using a compatibilizer. Both PC and PP are nonconducting and for their use in EMI shielding applications different types of conducting nanoparticles must be incorporated into the system. Thomas and co-workers [27] used a PC/PP

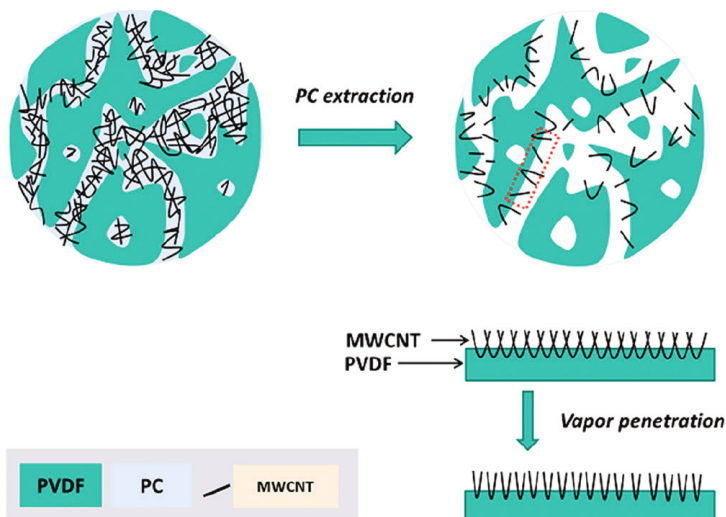
polymer blend system in EMI shielding applications. They used MWCNT to induce conductivity in the immiscible system, and as a means to compatibilize the immiscible system, and PP-grafted maleic anhydride (PP-g-MA) as a compatibilizer. A schematic of the morphological evolution in the presence of the compatibilizer and the MWCNT is shown in Figure 1.2



**Figure 1.2** Schematic illustration of the morphological evolution of PC/PP/PP-g-MA/MWCNT nanocomposites. Reproduced with permission from [27]. Copyright 2018, American Chemical Society

The mechanisms in which immiscible polymer blends in the presence of a number of nanomaterials will be explicitly elaborated in **Chapter 8** of this book. PC can also be blended with PVDF in the presence of CNTs to make templates that can be used to attenuate electromagnetic radiation [28]. Pötschke and co-workers also blended PC with PVDF to establish a co-continuous morphology that was used in sensor applications [29]; different PCs with varying molecular weights were used. In another strategy, the PC phase was extracted, and the MWCNT was left exposed on the surface of the PVDF, as illustrated in Figure 1.3. The establishment of immiscible polymer blend systems in the presence of conducting nanomaterials is an effective method to reduce the cost of fabricating conducting composites.





**Figure 1.3** Sensing mechanism illustration of porous sensors based on co-continuous PC/PVDF/MWCNT blend composites in which PC was selectively extracted. Reproduced with permission from [29]. Copyright 2020, American Chemical Society

To prevent environmental impact, recycled PC can be blended with PE, and the resultant polymer blend system can be used in different applications. Blending these two polymers will be of great importance to protect the environment and save money. To improve the compatibility of the two polymers, compatibilizers such as oxidized PE (OPE) can be used [30]. The use of OPE improves the mechanical properties of the overall blend system enabling it to be reused in other different applications. Besides OPE, CNTs can also be used in PP-based immiscible polymer blends as compatibilizers [31].

## ■ 1.4 Biobased Polymer Blend Systems

An increase in plastic pollution has recently resulted in researchers focusing more on biobased polymers. Biobased polymers can either be biodegradable or nonbiodegradable. Even though most biobased polymers are environmentally friendly, their main challenge is that they are very expensive to produce. It would be of great significance to develop state-of-the-art technologies that produce relatively cheap bioplastics. In a study conducted by Misra, Mohanty, and co-workers, they mixed poly(trimethylene terephthalate) (PTT), a biobased polymer, and biobased PE (BioPE) [32] and observed an improvement in the impact strength of the new biobased blend. PTT was reported to have comparable properties to that of poly(eth-

ylene terephthalate) and poly(butylene terephthalate) [33]. PTT has several properties, such as good dimensional stability, less water absorption, and good chemical resistance, which makes it favorable to be used in different applications. PLA is also one of the widely used polymers, especially in food packaging applications. The major shortfall of PLA is that it is very expensive, and to reduce the cost, it can be blended with another biobased polymer such as starch. Both starch and PLA can be blended, taking advantage of their individual unique properties. Starch is cheap and readily available; hence can be a useful polymer in reducing the purchase and production costs of PLA when blended. Even though starch and PLA form an immiscible polymer blend system, the interfacial adhesion can be improved by making use of compatibilizers. This improves the mechanical properties of the blend resulting in the blend being used in different applications. Different types compatibilizers of used in compatibilizing PLA/starch polymer blend can be found in Table 1.1.

**Table 1.1** Different Types of Compatibilizers Used in PLA/Starch Blend Systems

Compatibilizer	Reference
Methylene diphenyl diisocyanate	[34]
Diocetyl maleate	[35]
Poly(vinyl alcohol)	[36]
Poly(hydroxyester-ether) (PHEE)	[37]
Poly(lactide)-graft-glycidyl methacrylate (PLA-g-GMA)	[38]
Maleic anhydride (MA)	[39]

Chitosan is another abundant biobased polymer that has been used in packaging applications. Its main disadvantage is that it readily absorbs moisture, and this shortfall can be repressed by mixing it with a polymer that has good moisture barrier properties. Blending chitosan with a hydrophobic polymer such as PLA can significantly improve its applications [40].

## ■ 1.5 Industrial Significance and Commercial Applications of Different Polymer Blend Systems

The performance of polymer blends in different applications is mainly determined by the properties of the two blended polymers, the presence of nanomaterials, and the resultant morphology of the phase-separated polymer blend system. The appli-

cation of different types of polymer blend systems will be extensively investigated in **Chapter 9** of this book. In this section, a summary in table form of different kinds of polymer blends and their state-of-the-art applications are presented in Table 1.2.

**Table 1.2** Recent State-of-the-Art Applications of the Polymer Blend Systems

Blend System	Application	Reference
PS/PVME	Electromagnetic shielding	[41]
PS/PVME	Antibacterial membranes	[42]
PVDF/PMMA	Suppressing electromagnetic radiation shielding	[43]
Poly(3-hexylthiophene-2,5-diyl) (P3HT) and (PMMA)	Nitrogen dioxide sensors	[44]
PVDF/PMMA	Water remediation	[45]
Polyacrylonitrile(PAN)/polyurethane (PU)	Water purification	[46]
Poly(dimethylsiloxane)/polystyrene	Optical oxygen sensors	[47]
Polypropylene (PP)/poly(ethylene terephthalate) (PET)	Electromagnetic radiation shielding	[48]
Polyvinylpyrrolidone/hydroxy-propyl-methylcellulose acetate succinate	Drug delivery	[49]
Poly(L-lactide-co-D,L-lactide)/poly(acrylic acid)	Tissue engineering	[50]

## ■ 1.6 Conclusions

Polymer blends can be categorized into miscible and immiscible polymer blends depending on the specific interaction between the two polymers. The blending of two polymers has been shown to have various advantages, such as the development of materials with the desired set of properties at a relatively low cost. The effect of different types of nanomaterials on the demixing temperature, segmental dynamics, and morphology evolution of different types of polymer blends was explored in this introductory chapter. The advent of polymer blends has played a significant role in developing multiphasic structures that can be used in different state-of-the-art applications such as water remediation, drug delivery, and electromagnetic radiation shielding, to mention a few. These applications are of great importance in improving the lifestyle of humankind and in improving existing technologies. The following chapters will explicitly dwell on different types of phase

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