Chapter 2
Role of Functional Polymers in the Compatibilization of Polymer Blends

Ajitha Anthickamalil Ramachandran, Arunima Reghunadhan, Hanna J. Maria, and Sabu Thomas

Abstract Polymer mixing is one of the direct and practical strategies for creating new superior materials for commercial and industrial applications. The polymer blend can reinforce the setting of the properties according to the focused need. The compatibility of the immiscible polymer mixing system by incorporating a new material, helps in the development of high-performance materials. In general, graft, block or random copolymers have widespread applications as compatibilizers. Compatibilization is based on a specific chemical reaction between two functional polymer components during mixing, and is known as a reactive mixing. The introduction of reactive and functional polymers into an immiscible polymer blend with a strong interaction between the two polymer components of the mixtures can improve the adhesion between the components. Functional polymers have significant importance because of the high compatibilizing efficiency since the compatibilizer is created directly between the interfaces. In this chapter the interfacial reaction and morphology, the effect of reactive polymers on the polymer mixing process, the relationship between the flow field or process parameters, the compatibilizing efficiency of a reactive compatibilizer in different mixing techniques will be discussed. The concept of reactive compatibilizer, the characterization techniques used to monitor the compatibility of functional polymers, future perspectives and challenges in this field will also be discussed in this chapter.

Keywords Characterization · Grafting · Immiscible polymers · Polymer thermodynamics

A. A. Ramachandran · A. Reghunadhan · H. J. Maria
International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, Kerala, India

S. Thomas (✉)
International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, Kerala, India

School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India
e-mail: sabuthomas@mgu.ac.in

2.1 Introduction

Polymer mixtures is the combination of two or more polymers. Polymer mixing is an effective method to fabricate a new material with combined properties of both components. It is an efficient strategy to make a new material profitable other than synthesizing a new one. It can generally be said that polymer mixtures are physical mixtures of two or more polymers with chemical and physical interactions. Polymer mixing can be considered as a cost-effective method for the development of a material with specific properties according to customer requirements (Bahrami et al. 2015; Chiu 2017; Otero-Navas et al. 2017; Wang et al. 2017; Utracki 1982; Roman et al. 2017; Paul and Newman 1978; Brown 2003). Polymer mixtures can be classified into three types depending on the miscibility between the components, such as miscible, compatible and immiscible mixtures. Miscible mixtures are of a homogeneous nature and show properties of individual components (Lu and Weiss 1992), while immiscible mixtures are heterogeneous. The miscibility of polymer mixtures depends mainly on the chemical nature of the polymers, the interaction between the polymer components, the interfacial tension and the polarity of polymer components. Miscible mixtures will obtain negative free energy of mixture (Gibbs-Helmholtz equation - $\Delta G_m = \Delta H_m$ - T. ΔS_m) (Zarrintaj et al. 2019). Some examples of miscible polymer mixtures are poly(styrene)/poly(phenylene oxide) (PS/PPO) and poly(styrene-acrylonitrile)/poly(methyl methacrylate) (PSAN/PMMA) (Thomas and Grohens 2014).

Compatible mixtures have a fine phase morphology and show better properties even though they are not completely miscible. Polymer mixture from acrylonitrile-butadiene-styrene (ABS)/poly(carbonate) (PC) involved in this category (Tjong and Meng 2000). Due to the large difference in polarity and viscosity between the individual polymer components and due to the absence of chemical interaction between individual polymer components, most mixtures are immiscible with a heterogeneous phase structure. The immiscible mixtures acquire clear interfaces due to the great interfacial adhesion between the components and the poor interfacial adhesion between the components. The real reason for the immiscibility based on thermodynamics sheds light on the insignificant entropy of the mixture (ΔS_m). Some examples include mixtures from poly(ethylene terephthalate)/poly(vinyl alcohol) (PET/PVA), poly(butylene terephthalate)/PS (PBT/PS), poly(propylene)/PS (PP/PS), PP/poly(ethylene) (PP/PE), PC/PP and PP/poly(trimethylene terephthalate) (PTT), etc. (Thomas and Grohens 2014; Arif et al. 2017; Mathew et al. 2018).

Four basic morphologies can be expected for miscible mixtures, such as co-continuous morphology, droplet/domain morphology, fiber-like morphology and lamellae morphology. Most mixtures exhibit co-continuous and domain morphologies. Co-continuous morphology can be defined as the coexistence of two or more continuous structures within the same amount, while the droplet/domain morphology means the dispersion of the minor phase (polymer phase with low concentration) on the major continuous phase (polymer phase of high concentration) (Pötschke and Paul 2003; Gergen et al. 1987).

2.2   Thermodynamics of Binary Polymer Mixing Systems

As already discussed, most polymer mixtures are thermodynamically immiscible and incompatible by nature. The miscibility of polymer mixtures can be predicted using thermodynamic relations through the Gibbs free energy of mixture (ΔG_m), i.e. miscible polymer mixtures satisfy the following equations:

$$\Delta G_{\mathrm{m}} = \Delta H_{\mathrm{m}} - \mathrm{T}.\Delta S_{\mathrm{m}} < 0 \tag{2.1}$$

$$\left(\frac{\partial^2 \Delta G_m}{\partial \Phi_i^2} \right)_{T,p>0} \tag{2.2}$$

where, ΔG_m is the free energy of the mixture *per* unit volume and ΔH_m and ΔS_m are enthalpy and entropy of the mixture, respectively, while Φ_i represents the volume fraction of the component, and p and T represent fixed pressure and temperature, respectively. Generally, the ΔS_m is very low due to the macromolecular size. The ΔG_m is thus more positive due to the important contribution of the positive ΔH_m. Miscible mixtures can be formed if the entropic contribution exceeds the enthalpic contribution. So, for the negative ΔG_m values, there must be excellent intermolecular interactions between the components (Paul and Barlow 1984; Robeson 2007). The general phase diagram showing the variation in ΔG_m for miscible, immiscible and partially miscible mixtures is given below in Fig. 2.1.

The mixtures of immiscible polymers do not satisfy Eqs. 2.1 and 2.2, and have positive ΔG_m values, which represents the curve 'a'. Miscible mixtures satisfy the above equations and represent as the curve 'b' in the phase diagram. The curve 'c' represents a partially miscible mixing system (Ajitha and Thomas 2020).

Fig. 2.1 Free energy of mixture for: (**a**) completely immiscible mixtures, (**b**) completely miscible mixtures and (**c**) partially miscible mixtures. Reproduced with permission from Ajitha and Thomas (2020)
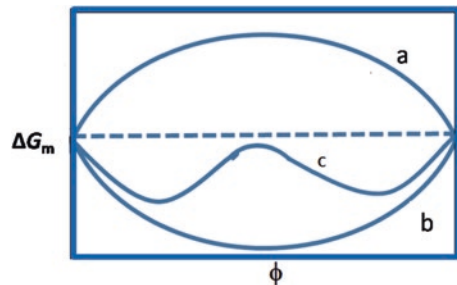
2.3 Purpose of Compatibilization

Most polymer mixtures are thermodynamically immiscible and incompatible. Therefore, poor and inferior properties can be expected compared to individual components, and their applications are limited. The poor properties of incompatible mixtures are due to the great interfacial tension and the poor interfacial adhesion between the components The immiscibility and incompatibility result in an unstabilized morphology, phase separation and poor interfacial adhesion between the polymer components, because of this, the mixtures show poor physical-mechanical properties. In general, the compatibilization method is used to overcome these problems and improve the applications of the mixtures. The compatibilization can be carried out using compatibilizers, which are interfacial agents that can be aligned along the interfaces between the two polymeric phases, thus reducing the interfacial tension. Thus, due to the interfacial activities of the compatibilizers, there are opportunities to improve the interfacial adhesion between the components, and therefore, to improve the compatibility between the components with the stabilized morphology. It can thus be said that compatibilizers play a fundamental role for improving the properties of immiscible and incompatible polymer mixtures by improving interfacial adhesion between polymer components.

Block, graft or random copolymers are generally used as compatibilizers for compatibilizing thermodynamically immiscible and incompatible mixtures (Bharati et al. 2017a, b). Immiscible and incompatible binary mixtures can be prepared, using a compatibilizer so that one segment is miscible or interacts with one phase of the mixture, while the other miscible segment interacts with the second phase of the mixture. As a result, compatibilizers are found in the interfaces of the mixtures and their interfacial activities result in better adhesion between the components by producing a useful product with improved properties (Bharati et al. 2017a, b).

2.4 Thermodynamic Theories

The compatibilization action of compatibilizers is similar to that of an emulsifier (Saleem and Baker 1990; Sinha Ray and Bousmina 2005; Utracki 2002; Wang et al. 2003). Noolandi and Hong (1982, 1984) studied the emulsifying effect of compatibilizers. Noolandi (1984) noted the importance of the copolymer concentration and molecular weight (Mw) in reducing the interfacial tension between the polymer components in the case of highly incompatible polymer mixtures. Leibler's theory means almost compatible systems. Leibler (1982) studied the interfacial properties of copolymer polymer mixtures and developed midfield formalism. Hong and Burns (1971) also developed the role of concentration and Mw of compatibilizers to

improve interfacial adhesion between polymer components in the polymer mixture. Hong and Burns (1971), Noolandi and Hong (1982, 1984) and Noolandi (1984) reported that as the concentration and Mw of the copolymers increases, the interfacial tension decreases. While at a particular concentration (critical micelle concentration - CMC) of copolymer produces interfacial saturation and particle size is leveled (interfacial saturation). No further changes in the interface can be observed with the addition of copolymers above CMC, but it leads to the formation of copolymer micelles in homopolymer phases.

According to Hong and Burns (1971), Noolandi and Hong (1982, 1984), Noolandi (1984), Thomas and Prud (1992) and George et al. (1995) for ternary systems of two polymers A and B with copolymer A-*b*-B (A/A-*b*-B/B), the reduction of interfacial tension can be expressed by the following equation:

$$\Delta\gamma \cong d\varphi_c \left[1/2\chi + 1/Z_C - 1/Z_C \exp\left(Z_C \chi / 2\right) \right] \tag{2.3}$$

where ϕ_c represents the bulk volume fraction of the copolymer, χ represents the Flory-Huggins interaction parameter between the two segments of the copolymer, d represents the width of half the height of copolymer profile and Z_C represents the degree of polymerization of the copolymer. According the above equation, the reduction or increase in particle size (ΔD) can be written as:

$$\Delta D \cong K d\varphi_c \left[1/2\chi + 1/Z_C - 1/Z_C \exp\left(Z_C \chi / 2\right) \right] \tag{2.4}$$

where K is proportionality constant.

Figure 2.2 shows the mechanism of compatibilization of a copolymer A-*b*-B within an immiscible mixture, the yellow part of the copolymer has more affinity with the A polymer segment, while the blue part interacts selectively with the B polymer segment (Dal Lago et al. 2019; Ajitha and Thomas 2020).

During compatibilization, compatibilizers migrate to the interface between the components and interact with the polymer components. This action of compatibilizers helps reduce the dimensions of the dispersed phase, thus stabilizing the morphology of the mixture and improving the adhesion between the polymer components. Generally, graft, block copolymers and coupling agents are used as compatibilizers. Another important strategy for the compatibilization of immiscible mixtures involves the use of functional polymers, micro- and nanofillers and Janus nanoparticles (NPs). This chapter deals the role of functional polymers in the compatibilization of polymer mixtures.
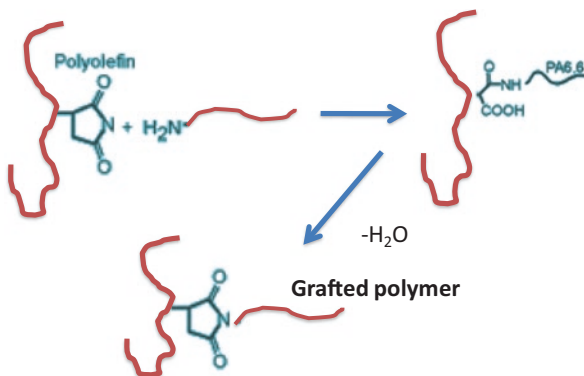
2.5 Functional Polymers in Compatibilization

In compatibilization, the widely used functional polymers are maleic anhydride (MA) and glycidyl methacrylate (GMA). Compatibilizers of this type usually contain some polar groups in addition to the reactive functionalities. Compatibilization
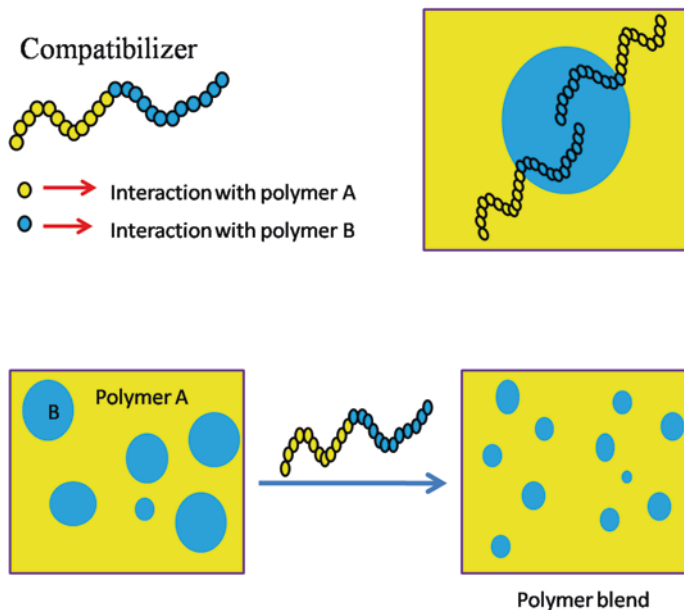
Fig. 2.2 Schematic representation of the compatibilization of a polymer mixture by block copolymers. Reproduced with permission from Ajitha and Thomas (2020)

Fig. 2.3 Schematic representation of a mixture system using compatibilizer

using functional polymers is given under *ex-situ* compatibilization conditions. Reactive rubbers are also considered compatibilizers. The compatibilized system having a reactive functional polymer as a compatibilizer can be represented in Fig. 2.3.

2.6 Characterization of Composites Involving Functional Polymers

Polymer composites and compatibilized mixtures can be characterized by several methods. Compatibilization usually introduces some kind of miscibility and interaction between the two polymers in a mixing system.

2.6.1 Structural Characterization

The compatible mixing system can be studied for the interfacial reaction by a series of techniques. Spectral studies, including nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectra, are the most widely selected techniques. Special techniques including neutron reflectivity and forward recoil spectrometry (FRES), labeling of a functional polymer with a fluorescent group, etc.

Urethanes can, for example, be considered as a model compound to explain the process of reactive compatibilization. The –NHCOO and –NCO group into thermoplastic polyurethanes are reactive to most functional polymers. Urethanes react with acids, amines, anhydrides, epoxides, etc. Lu et al. (2002) used NMR spectra to control the reaction of urethanes with the functionalities mentioned above. The NMR spectra of the compatibilized systems showed a peak around 0.06 ppm, which was protected by the imide formed by the reaction between the urethane and the anhydride (Fig. 2.4).

Dal Lago et al. (2019) used FTIR spectroscopy for analyzing the changes in the PC/PET mixture system by adding a methylene diphenyl diisocyanate (MDI) compatibilizer. After extrusion using MDI, the FTIR spectra exhibited changes other than the previous ones. The vibrations around 2250 cm^{-1} and 1590 cm^{-1} due to the isocyanate and amide functionalities, both improved with the MDI content. Therefore, the effect of compatibilization for a binary mixture can be well understood by continuously monitoring the variations of reactive functionalities (Fig. 2.5).

2.6.2 Morphology

Morphology control is one of the most important properties when polymer mixtures and composites with superior properties are developed. Uncompatibilized mixtures show a clear interface and the particle size is larger (Kudva et al. 1999a). This means that the uncompatibilized mixing system follows the same structure and morphology of an immiscible system. This statement can be explained by considering a
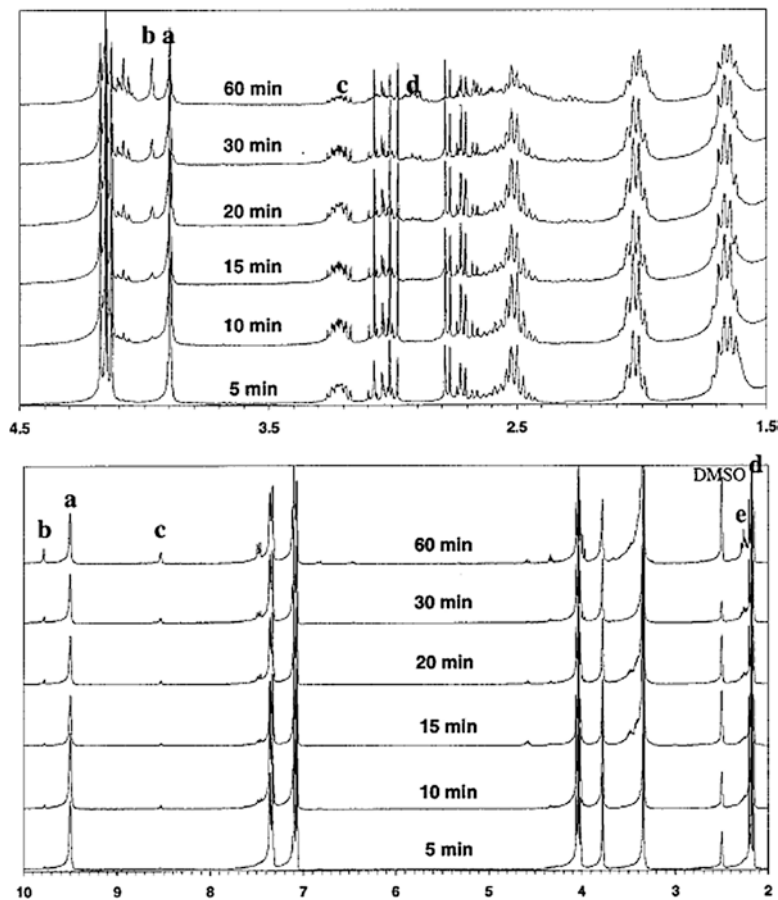
Fig. 2.4 Monitoring the reaction of urethane with a primary amine (**a**) and an acid (**b**) using ^{1}H NMR spectra. Reproduced with permission from Lu et al. (2002)

simple example of a binary mixing system formed from poly(amide) (PA) and PS. In this sense, Kudva et al. (1999a) showed that binary mixing systems had an average domain size of 30 μm, while the use of styrene-GMA as a compatibilizer, was shown to decrease the domain size and interfacial tension of the mixtures (Fig. 2.6). PA polymers are usually compatibilized by reactive functionalization and/or using reactive and functional polymers. In particular, the styrene-GMA pair is considered the most preferred compatibilizing agent for the immiscible polymer mixing system (Kudva et al. 1998). This compatibilizing pair has been used to compatibilizer mixtures made from PA/PS, PET/PS, PBT/PS, PBT/PPO, etc. (Hu et al. 1996; Liu et al. 1996).
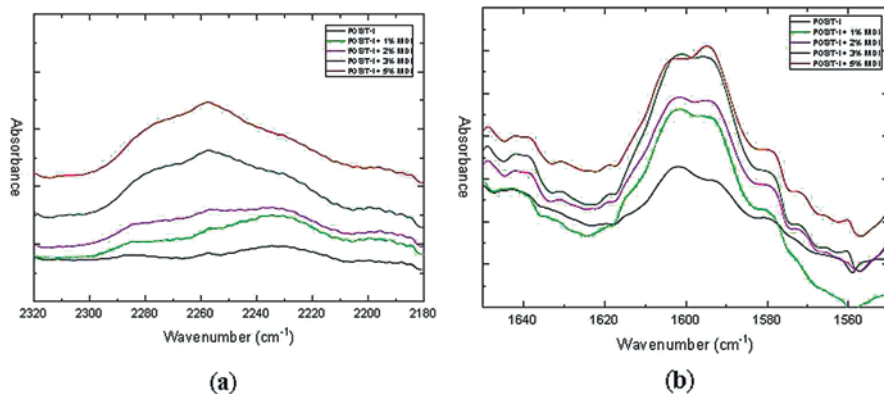
Fig. 2.5 PC/PET mixtures with and without the use of MDI as a compatibilizer. Reproduced with permission from Dal Lago et al. (2019)
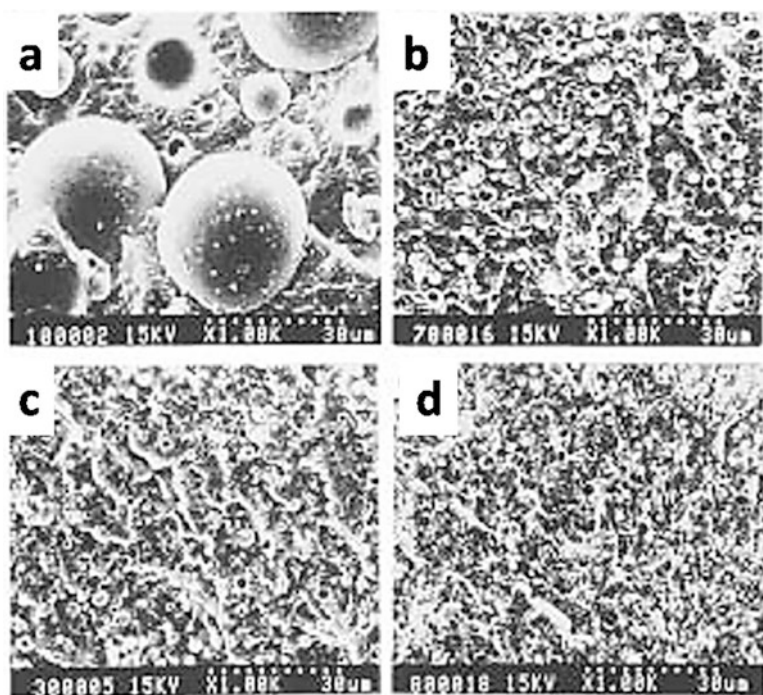
Fig. 2.6 Scanning electron microscopy (SEM) images of PA mixtures using styrene-GMA as a compatibilizer. Reproduced with permission from Kudva et al. (1999a)

Fig. 2.7 Different types of interfacial morphology developed during compatibilization using functional polymers: (**a**) interfacial roughness, (**b**) interfacial pinch-off and (**c**) microemulsion formation
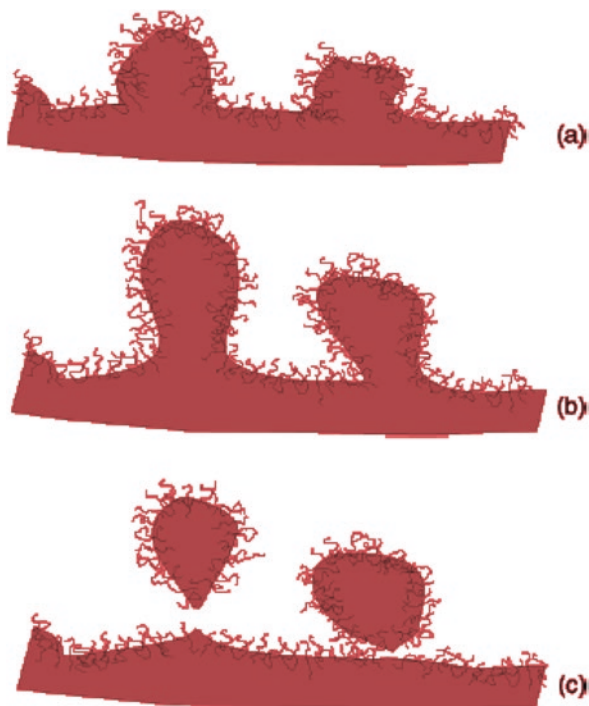

On the other hand, the morphology change at the interface can be divided into three: (a) interfacial roughness, (b) interfacial pinch-off and (c) microemulsion formation (Fig. 2.7). For example, Larocca et al. (2005) used low Mw methyl methacrylate (MMA)/GMA/ethyl acrylate (EA) terpolymer (MGE) as a compatibilizing agent, which led to the formation of micelles and/or microemulsions in the PBT/styrene-acrylonitrile (SAN)/MGE mixture (Fig. 2.8).

Macosko et al. (2005) conducted a detailed investigation of the reactions of functional polymers at the interface. These authors explained that the interfacial reactions can be increased by selecting certain pairs for compatibilization. The common pairs for this purpose are acid/amine, acid/epoxy, acid/oxazoline, aliphatic amine/anhydride, aliphatic amine/epoxy, anhydride/aromatic amine, aromatic amine/epoxy and hydroxyl/(anhydride or acid) (Fig. 2.9) (Macosko et al. 2005).

2.7 New Challenges

The compatibility of a mixture made from naturally immiscible polymers is an important academic and technological challenge. An example of this is the compatibility of petroleum-based polymers with biobased polymers, in order to reduce the carbon footprint of the final material, while maintaining the outstanding
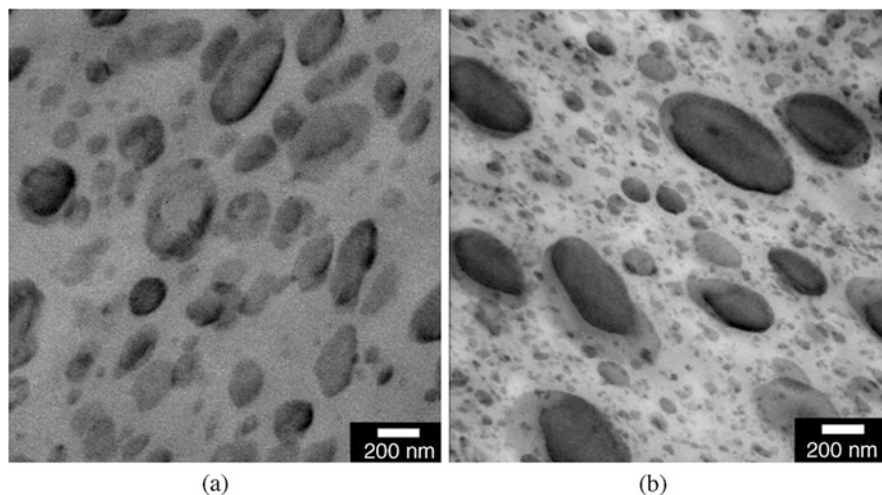
Fig. 2.8 Formation of microemions using MGE as a compatibilizing agent into the PBT/SAN mixture. Reproduced with permission from Larocca et al. (2005)
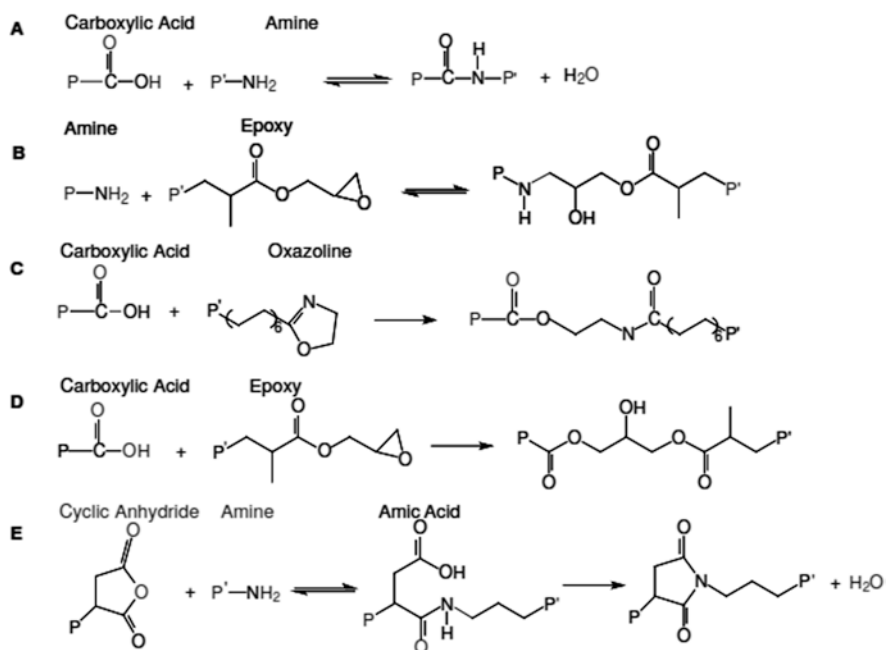

Fig. 2.9 Possible reactions between different functional groups. Reproduced with permission from Macosko et al. (2005)

thermomechanical properties of the final mixture. Another main challenge is with the recycled material, since in many cases, it is very difficult to predict the exact mixture of resins in any feed flow, and nowadays there is no 'one-size-fits-all' compatibilizer in the market for any mixture of materials. It is also mentioned from the literature that the optimal properties of the polymer mixtures are often based on an average dispersed-phase diameter less than several microns. Therefore, the stabilization of the dispersed-phase domain size against thickening is key to processing immiscible mixtures.

Among the compatibilization strategies tested so far, most involve a reduction in interfacial tension and/or steric hindrance against coarsening. The addition of block/graft copolymers normally leads to compatibilization, but this has not been commercialized, due in part to the very low CMC that prevents enough copolymer from reaching interface regions during melt processing. The addition of random copolymer leads to the encapsulation of the dispersed phase, and therefore, does not lead to compatibilization even in small-scale studies. There are some new approaches that can be studied to further expand the significance of compatibilizers. In one strategy, the gradient copolymers dispersed into homo polymer have much higher CMCs, and exhibit a broader interfacial coverage than block copolymers of the same composition, thus suggesting that gradient copolymers may be effective mixing compatibilizers. Other studies are have been carried out with functional compatibilizers and are preferred in the compatibilization of nanomixtures (mixtures of
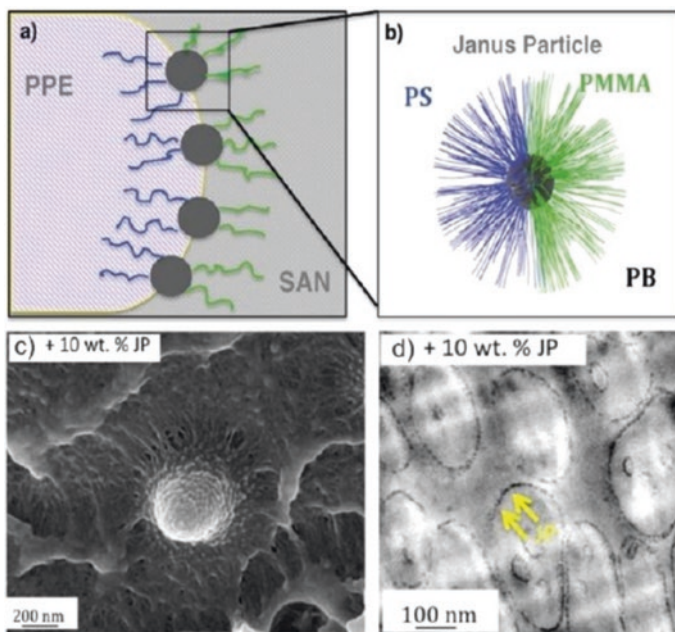
Fig. 2.10 Schematic illustration of SEM and transmission electron microscopy (TEM) images of Janus NPs at the interface. Reproduced with permission from Kirillova et al. (2019)
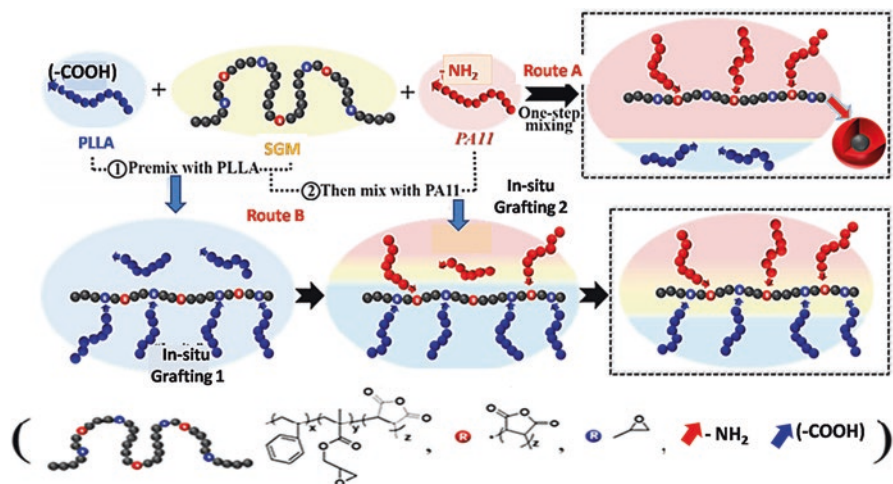
Fig. 2.11 Schematic representation of the compatibilization mechanism of PA11/PALLA. Reproduced with permission from Yang et al. (2019)

immiscible polymers in which the dispersed phase has particles with a size of 100 nm or less). In order to obtain nanostructured polymeric system, an attractive method is the inclusion of Janus NPs (J NPs), in which the surface is composed of hydrophilic groups and hydrophobic groups, resulting in asymmetric NPs able to act as surfactants in immiscible mixtures (Fig. 2.10) (Kirillova et al. 2019).

'Dual-reactive compatibilization' is another recent development in this area. This strategy uses a compatibilizer containing bi-functional groups. It has been shown that a compatibilizer containing two types of reactive groups shows greater compatibilization efficiency compared to the traditional compatibilizer with only one type of reactive groups. With this in mind, Yang et al. (2019) reported a series of poly(styrene-*co*-GMA-*co*-MA) ternary copolymers (SGM) containing both reactive epoxide groups and MA groups were synthesized and then incorporated into the immiscible poly(amide 11)/poly(L-lactic acid) (PA11/PLLA) mixture (Fig. 2.11) (Yang et al. 2019).

Another strategy in the reactive compatibilization is the use of thermo-oxidative synergistic maleation of the polymer. The synergistic action of maleation coupled with thermo-oxidation of the polymer backbone allows both improvements in hydrophilic/hydrophobic balance and availability of functional groups that can react during the reactive extrusion. Keeping this in view, Jubinville et al. (2019) investigated the maleation process of PA11, resulting in a multifunctional compatibilizer due to partial thermo-oxidation. The incorporation of PA11C into PA6/PBT mixtures promoted grafting reaction and resulted in better compatibilized mixtures (Jubinville et al. 2019).

2.8 Conclusion

Compatibility is a term related to the miscibility of the polymer. Several methods and theories have been developed to achieve the compatibilization process, which depend on the thermodynamics of polymer mixtures. The compatibility process is generally performed to improve the interfacial adhesion between the immiscible polymers. Polymers or fillers having reactive functionalities are preferred for this purpose. Functional polymers are an important part in compatibilization, followed by *ex-situ* mechanisms. The addition of functional polymers leads to a chemical reaction which improves miscibility and properties. The reactions can be controlled using spectroscopic techniques in which one can have a detailed analysis of the scope of the compatibilization process by analyzing the variation of the functional groups. The change in morphology at the interface is generally controlled by microscopic techniques. This chapter covered the theories and techniques mentioned above in detail and examined the latest trends or strategies in the compatibilization process. The use of block copolymers, Janus particles and the development of nanostructures are recent trends in compatibilization.

Conflicts of Interest The authors declare no conflict of interest.

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