THERMOPLASTIC-THERMOSET NANOSTRUCTURED POLYMER BLENDS

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CHAPTER OUTLINE HEAD

2.1 INTRODUCTION

A thermoplastic is a form of polymer that becomes soft or molten and pliable when heated and returns to a solid state on cooling without a change in its intrinsic properties. The heating and cooling can be repeated over and over again allowing reprocessing, reuse, and recycling [1]. Thermoplastic polymers are widely used in several industries such as automobile, building construction, aerospace, aviation industries, just to mention a few. The consumption of thermoplastic materials is roughly 80% of the total plastic consumption [2]. There are several types of thermoplastics but the most commonly used ones include polypropylene (PP), polyethylene (PE), high-density polyethylene, low-density polyethylene, linear low-density polyethylene, polystyrene (PS), poly(vinyl chloride), ethylene propylene diene monomer (EPDM), styrene acrylonitrile (SAN), polyamide 6 (PA6), polycarbonate (PC), poly(ethylene terephthalate) (PET), poly(p-phenylene oxide) (PPO), poly(butylene terephthalate), acrylonitrile butadiene styrene (ABS) and poly(methyl methacrylate) (PMMA) [3]. Products manufactured with them include water and soda bottles, packaging containers, safety glass lenses, children's toys, window frames, grocery bags, piping, airplane armrests, and footwear. Thermoplastic polymer resins are extremely common, particularly in an unreinforced form having shapes but no reinforcement to provide strength [4]. However, the increasingly demanding applications require improved or new combinations of properties, which cannot be satisfied by these few polymers alone. There has, therefore, been considerable scientific and industrial interest in modifying and mixing together these existing commodity polymers with a view to achieving the properties currently exhibited only by more expensively engineered polymers or non-polymeric materials [5]. Polymer blends based on thermoplastic polymers have been widely studied due to the important role each of the constituent polymer plays and the studies have included their mechanical properties, thermal properties, morphology, and rheology [6]. Polymer blends having controlled structures and distributions of phase separated domains on the nanometre scale are of particular interest since these materials may have desirable or tuneable physical properties [7]. Fabrication of polymer blends with nanometer-scale structure could lead to design and production of low-cost materials with valuable properties. Nanostructure polymer blends having a minority polymer phase with nanoscale dimensions offered much promise because of enhanced thermo-mechanical properties, optical transparency, and toughness in comparison to conventional polymer blends [8]. Specific electronic, mechanical, or optical properties could be achieved through this means for large-scale industrial applications and scientific solutions. These properties could be attributed to presence of particles with structures that have dimensions in nanometer range with inherently high surface-area-volume ratio [8]. When high surface-volume ratio materials are required, nanoparticles are often the first choice, but introducing nanoscale texture/features on nano- or micro-sized materials will also further increase the surface-volume ratio [9]. For the past three decades, there has been an increase in the usage of nanoparticles with polymer blends in which polymer blends act as the matrices for either individual research or industrial development [10–20]. The following are the most used nanoparticle fillers: layered silicates (montmorillonite), silica nanoparticles, nanotubes (mainly carbon nanotubes), metal nanoparticles (Au, Ag), polyhedral oligomeric silsesquioxane (POSS), metal oxides (TiO_2, Fe_2O_3, and Al_2O_3), carbon nanomaterials (graphene, carbon black) [21–30]. The major challenge is to overcome the inherent immiscibility of polymers by using compatibilizing agents to allow for a sufficient mixing into nanoscopically sized domains of the dispersed phase; this is handled by reactive blending or the addition of block copolymers as compatibilizer for the two components [4].

Denchev and Dencheva [31] stated three basic requirements that a composite material must satisfy so that it can be useful for engineering applications. The first one is the material must consist of at least two physically distinct and mechanically separable materials, which, depending on their properties and amounts used, are called matrix and reinforcing components. The second requirement is that there must be a possibility for its preparation by admixing of the above components (sometimes preceded or accompanied by some special treatment so as to achieve optimum properties). The third requirement is that there should be a kind of synergistic effect whereby the resulting material should give a better property than that of the individual components. For this to be achieved; distribution of the size and dispersity of the reinforcing component within the matrix must be reproducible; there must be a good adhesion and compatibility of the separate phases forming the composite. These depend on the presence of chemical and/or physical interactions at their interface. If the said interactions are negligible, because of the inherent immiscibility in polymer blends as a result of low entropy of mixing, mixing normally results in phase separation and technologically incompatible systems with insufficient mechanical properties. Should either chemical reactions or physical interactions at the interface play a major role, blending may cause better adhesion at the matrix-reinforcing element boundary. This could lead to the desired synergism in the composite properties and even generate materials with unique properties.

In this chapter the different ways of fabrication of thermoplastic-thermoset nanostructured blends, where thermoplastic is the matrix, will be discussed. The issues of phase separation and morphology shall be treated together with the properties of the blends and conclusions will be drawn.

2.2 **POLYMER BLENDS**

Polymer blend is a mixture of at least two polymers or copolymers. Polymer blends are physical mixtures of two or more polymers with or without any chemical bonding between them. Polymer blending is the process of mixing two or more different polymers together to form a new class of material with different physical properties [32]. The gradual depletion of economic ways of developing new monomers led to the development of polymer blending, also because newly developed monomers gave increase to polymers with intermediate properties as compared with individual polymers [33].

2.2.1 **TYPES OF POLYMER BLENDS**

When two or more polymers are mixed, the phase structure of the resulting material can be either miscible or immiscible. Polymer blend can be classified into three basic categories namely: miscible polymer blends, compatible polymer blends, and immiscible polymer blends [34]. The majority of polymers are immiscible at molecular level, as given by the laws of thermodynamics [35]. The internal disorder of the polymer system will eventually result in phase separation on a macroscopic scale after some time. The relative miscibility of polymers controls their phase behavior, which determines the final properties. Partially miscible blends show either two phases or single-phase morphology. However, the manifestation of superior properties depends on the miscibility behavior of homopolymer.

2.2.1.1 Homologous Polymer Blend

This type of blend is a mixture of two or more fractions of the same polymer, each of which has a different molar mass distribution. Any polydispersed polymer is a homologous polymer blend. These blends are miscible because of the closeness of molar mass distribution.

2.2.1.2 Miscible Polymer Blend

Miscible blends are homogeneous to the molecular level. For this type of blend, Gibbs free energy of mixing, $\Delta G_m \approx \Delta H_m \leq 0$ where ΔH_m is the enthalpy of mixing; and this is due to specific interactions. Homogeneity is observed at least on a nanometer scale, if not on the molecular level. This type of blends exhibits only one glass transition temperature (T_g), which is in between the glass transition temperatures of the blend components in a close relation to the blend composition [35]. Due to their high molar mass, the entropy of mixing of polymers is relatively low and, consequently, specific interactions are needed to obtain blends, which are miscible or homogeneous on a molecular scale. Most thermoset/thermoset blends are miscible over a very wide temperature range and in all compositions [36,37].

2.2.1.3 Immiscible Polymer Blend

Immiscible polymer blends are phase separated, with:

$$\Delta G_m \approx \Delta H_m \geq 0 \qquad (2.1)$$

where ΔG_m is the Gibb's free energy and ΔH_m is the enthalpy heat of mixing.

The overall physico-mechanical behavior depends critically on two demanding structural parameters. The first one is a proper interfacial tension leading to a phase size small enough to allow the material to be considered as macroscopically homogeneous and an interphase adhesion strong enough to assimilate stresses. The other is strains without disruption of the established morphology [35]. Fully immiscible blends have a coarse morphology, sharp interface, and poor adhesion between the blend phases. These kinds of blends show a two-phase morphology, so they are of no use without compatibilization. When blends are incompatible, the properties of the blend are inferior to those of pure polymers. But, most pairs of high-molecular-weight polymers are immiscible or incompatible. Polymer-polymer miscibility depends on a variety of independent variables which include composition, molecular weight, temperature, and pressure. Components, which resist gross phase segregation and show desirable blend properties, are considered to have a good compatibility, even though they are immiscible in a thermodynamic sense. These blends will exhibit different T_{gs} corresponding to the T_g of the component polymers. Examples of fully immiscible blends are PA/ABS, PA/PPO, PA/EPDM, and PA/PP. Now these blends have become commercially successful, after being efficiently compatibilized using suitable compatibilizers [35].

2.2.1.4 Compatible Polymer Blend

In this type, a small part of one of the blend component is dissolved in the other part, so the blend exhibits fine phase morphology and satisfactory properties. Both blend phases are homogeneous, and have their own T_g. Both T_g are shifted from the values for the pure blend components toward the T_g of the blend component. An example is the PC/ABS blends. In these blends, PC and the SAN phase of ABS partially dissolve in one another. In this case interface is wide and the interfacial adhesion is good [35].

2.2.1.5 Polymer Alloy

These are immiscible polymer blends with modified interface. Although they are heterogeneous in nature, their properties and morphologies are controlled by compatibilization. Dawson [38] described the composition of a polymer alloy he patented in 1991 which was a blend of PP, ethylene copolymer ionomer resin, ethylene/glycidyl acrylate, or methacrylate coplolymer. The polymer alloy was claimed to be useful in applications where a wide range of temperatures and abrasive conditions are encountered. Another example is Neoloy which composed of polyolefin and thermoplastic engineering polymer developed specifically for use in high-strength geosynthetics [39].

2.3 THERMOPLASTICS/THERMOSETS BLENDS IN A THERMOPLASTIC MATRIX

Thermoplastic matrix can be reinforced with short discontinuous fibers or continuous fibers. In order to improve the affinity and adhesion between fibers and thermoplastic matrices in production, chemical "coupling" or "compatibilizing" agents have been employed [40]. Both fibers increase the mechanical properties of the product but continuous-fiber-reinforced composites have significantly greater strength than discontinuous-fiber-reinforced composites. Recently, thermoplastic resins have been used with continuous fiber creating structural composite products. Thermoplastic composites have some distinct advantages and disadvantages against thermoset composites. Advantages of thermoplastic composites include an increased impact resistance to comparable thermoset composites. Another major advantage of thermoplastic composites is the ability to reform. Raw thermoplastic composites, at room temperature, are in a solid state. When heat and pressure are applied to impregnate a reinforcing fiber, a physical change occurs and not a chemical reaction as with a thermoset. This allows thermoplastic composites to be reformed and reshaped. This is not possible with thermosetting resins. This behavior also allows for the recycling of the thermoplastic composite after use. One disadvantage of thermoplastics is that it is much more difficult to impregnate reinforcing fiber because thermoplastic resin is naturally in a solid state. The resin must be heated to the melting point, and pressure is required to impregnate fibers, and the composite must then be cooled under this pressure. This is complex and very different from the traditional way of manufacturing thermoset composite. The process requires the use of special tooling, technique, and equipment, many of which are expensive [41].

Thermoplastics and thermosets form a highly incompatible blend due to their large differences in polarity and high interfacial tensions. However, these blends can reduce costs and improve the processability of thermoplastics. The mechanical, thermal, and chemical properties of thermoplastics are improved by blending it with thermosets [42]. Thermoplastics also increase the impact strength, adhesion, printability, and paintability characteristics of thermosets.

Polymeric materials are rarely used for applications in their pure form. They are often mixed with additives that alter their ability to be processed, modulus, impact strength, appearance, conductivity, or flammability. Moreover, tailoring of polymer bulk properties may be achieved by blending different polymers [43]. Adding solid particles in polymer blends is a traditional technique in rubber and thermoplastic processing. About 70% of polymer-based materials contain solid particles, fillers of different size from a few nanometers to micrometer [44,45]. Originally, the purpose

of adding particles in elastomer blends was obviously an applicative objective like obtaining high electrical conductivity or improving the mechanical properties [46,47]. Example of thermoplastic/thermoset nanostructured blends is nanostructured poly(vinylidene fluoride)/polyamide 11 (PVDF/PA11) blends.

2.4 **PHASE SEPARATION**

An emulsion is a mixture of two immiscible fluids in which one of the fluids is dispersed in the shape of droplets with a small size ranging from millimeters to less than 1 mm. Based on this definition, molten polymer blends may be considered as high viscosity fluid emulsions [46]. After homogenization, the immiscibility and incompatibility of the liquids may be the cause of macroscopic phase separation and, depending on the application, it is of the utmost importance that this does not occur [46,48]. Few polymers form truly miscible blends characterized by a single T_g and homogeneity at a 5-10 nm scale. The majority of blends are immiscible, which implies that they possess phase separated morphology [49]. Phase separation of polymer blends is as a result of the large unfavorable enthalpy of mixing, resulting to deterioration in mechanical properties [50]. Therefore, controlling the phase behavior and morphology becomes a key factor in converting these immiscible blends into useful polymeric products. Reducing phase size and improving interfacial adhesion is necessary for the practical application of polymer blends [51]. The traditional method to manipulate the interface properties of polymer blends is of adding some copolymers as compatibilizers [52]. In general, the added copolymers are compatible with both phases, thereby segregating preferentially at the interface and ensuring strong interfacial adhesion [50]. Addition of nanoparticles can reduce interfacial tension and improve miscibility between polymers and, thus, have a significant effect on phase behavior of polymer blends [53]. However, the effect of nanoparticles on the miscibility of polymer blends depends greatly on the interactions among particles and polymers, which influence the location of nanoparticles in the phase-separated blends [54]. Rheological measurements have been widely used to detect the phase separation, because rheology can link the viscoelastic response of polymer blends to subtle structural changes during phase transition regardless of the transparency and refractive indices of the components. Specifically, the viscoelasticity of polymer blends in the terminal region can be directly associated with the interfacial tension and characteristic length of domains. Huang et al. [54] demonstrated that nanoparticles retard coarsening of morphology during phase separation and this was mostly pronounced in off-critical blends with nanoparticles located on the interface. On the other hand, nanoparticles preferentially locating in the minor phase could act as nucleation sites but decrease the total number of nuclei. They also observed a difference in the rheological transition temperatures which was ascribed to the effect of nanoparticles on the components' viscoelasticity and the morphology during phase separation.

Polymer layers can exhibit significantly improved performances if they possess a multicomponent phase-separated morphology. Kietzke et al. [55] presented two approaches to control the dimensions of phase separation in thin polymer-blend layers based on polymer nanospheres prepared by the miniemulsion process. In the first approach, heterophase solid layers are prepared from an aqueous dispersion containing nanoparticles of two polymers, whereas in the second approach, both polymers are already contained in each individual nanoparticle. In both cases, the upper limit for the dimension of phase separation is determined by the size of the individual nanoparticles, which can be adjusted down to a few tens of nanometres. They also demonstrated that the efficiencies of solar cells using

two-component particles are comparable to those of devices prepared from solution at comparable illumination conditions, and that they are not affected by the choice of solvent used in the miniemulsion process. Insoluble particles such as silica, carbon black, metal oxides, or polymer latex have been proven to adsorb strongly at the fluid-fluid interface and are consequently able to stabilize even high viscosity emulsions like immiscible polymer blends [46].

2.4.1 COMPATIBILIZATION

Most pairs of polymers are immiscible with each other and, in addition to this, they have less compatibility than would be required in order to obtain the desired level of properties and performance from their blends. Compatibilizers are often used as additives to improve the compatibility of immiscible polymers in order to improve the morphology and resulting properties of the blend [56,57]. For example, methyl methacrylate, styrene, and maleic anhydride-based core-shell compatibilizer are being used to compatibilize immiscible PC/ABS blends [58]. Similarly, it is often challenging to disperse fillers effectively in the matrix polymer of a composite or to adhere the layers of the polymers to each other or to other substrates (such as glass or metals) in laminates [59]. Compatibilization is very useful for improving the dispersity in polymer blends. It reduces interfacial tension, facilitate dispersion, stabilizes the morphology against abusive stresses and strains as a result of processing, enhances adhesion between phases, and improves the overall mechanical properties of the products [20,60,61]. The driving forces for the phase segregation of blend components are gravity and interfacial tension. The rate of demixing depends on interfacial tension, viscosity, and density differences. Compatibilized blends are not necessarily miscible blends, but blends that satisfy certain industrial criteria for usefulness, such as satisfactory mechanical properties [35].

The key to solve problems of coarse morphology is to reduce interfacial tension in the melt and to enhance adhesion between the immiscible phases in the solid state. One solution is to select the most suitable blending technique so that co-continuous phase morphology can be obtained, which results in direct load sharing. The second solution is the addition of a third homopolymer or block or graft copolymer or low molecular reactive compounds, which is miscible with either of the two phases. This can be considered as non-reactive compatibilization. The third way is to blend suitably functionalized polymers, which are capable for specific interactions or chemical reactions (reactive compatibilization) [35].

2.5 CURING

The curing process induces reaction-phase separation and this has an effect on both the crystallization and morphology of thermoplastic/thermoset blends. Goossens and Groeninckx [62] studied the influence of the curing reaction on the crystallization and melting behavior of high melting thermoplastic/ epoxy resin blends. Their investigation was done at two curing temperatures: one lower than the melting point of the thermoplastic used (145 °C) and the other at higher temperature (180 °C). The thermoplastic used was polyoxymethylene (POM). They identified two distinct crystallized POM, which are dynamically and isothermally crystallized POM. Concerning the dynamically crystallized material, a clear difference could be made between the material crystallized in the homogeneous sample and that crystallized in the phase-separated structures. The isothermally crystallized POM was to a large

extent influenced by the conversion degree of the epoxy resin. Figure 2.1 shows the difference in phase morphology development for a 10 wt% POM blend and a 20 wt% POM blend, each cured at 180 °C. The final blend morphology differs depending on the initial blend composition with the 20 wt% POM revealing a co-continuous structure breaks up in epoxy-rich holes dispersed in the POM-rich matrix as shown in Figure 2.1c and d. However, for curing at 145 °C and at 20% POM, the epoxy-rich droplets dispersed in a POM-rich matrix are shown in Figure 2.2b.
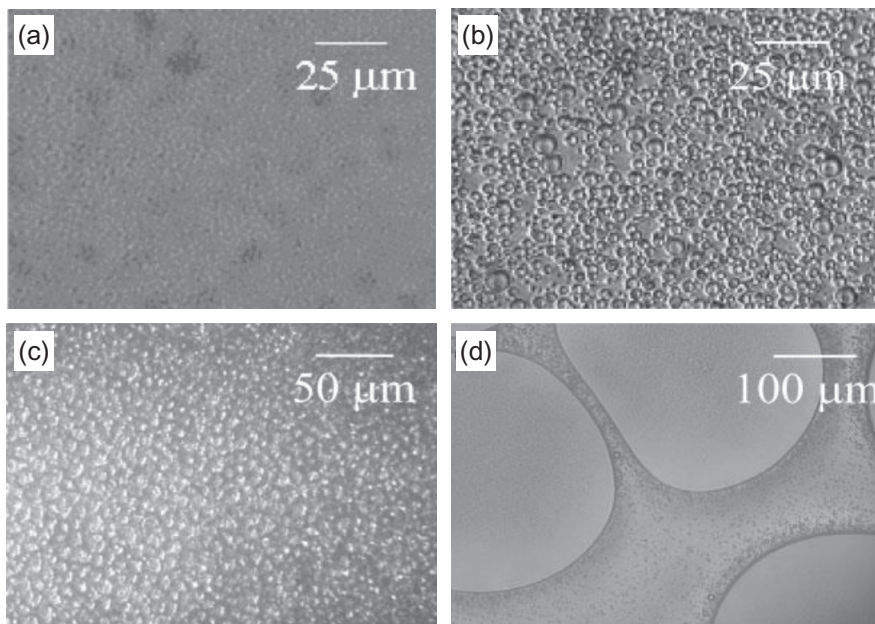

FIGURE 2.1

Optical microscopy pictures of the isothermal phase separation process of a 10 wt%. POM blend (a) after 11 min and (b) 14 min of curing at 180 °C, and of a 20 wt% POM blend (c) after 12 min and (d) 60 min of curing at 180 °C [62].
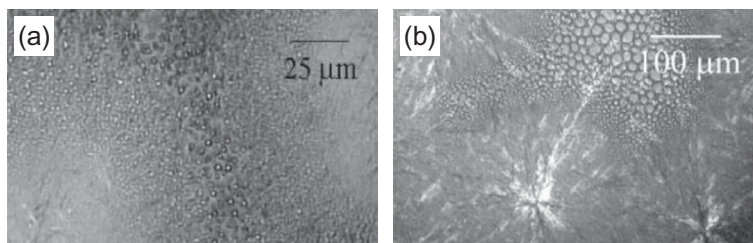

FIGURE 2.2

Optical microscopy pictures of the epoxy/POM blend morphologies of (a) a 10 wt% POM and (b) a 20 wt% POM blend, each cured for 1 h at 145 °C [62].

Tribut et al. [63] investigated the rheological behavior of atactic PS (85 and 60 wt%) blended to a stoichiometric mixture diglycidyl ether of bisphenol A (DGEBA) with 4,40-methylenebis(2,6-diethylaniline) during isothermal curing. After phase separation, the blend is biphasic, as can be seen from the transmission electron microscopy (TEM) pictures in Figures 2.3 and 2.4. When two phases are created, they are not pure. Some epoxy monomers or i-mers remain in the PS matrix while some short chains of PS are trapped in the epoxy-rich droplets.
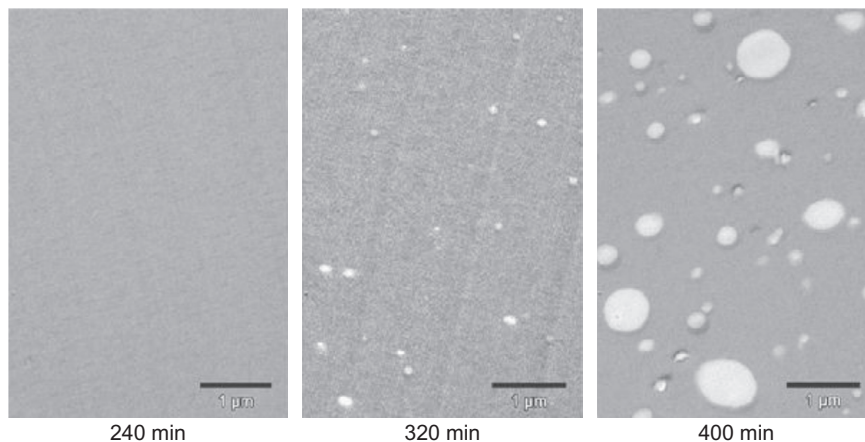

240 min	320 min	400 min

FIGURE 2.3

PS/DGEBAeMDEA 85/15 polymerized at 177 °C. Morphology of the blend at different reaction times (the epoxy-amine drops appear in light gray) [63].

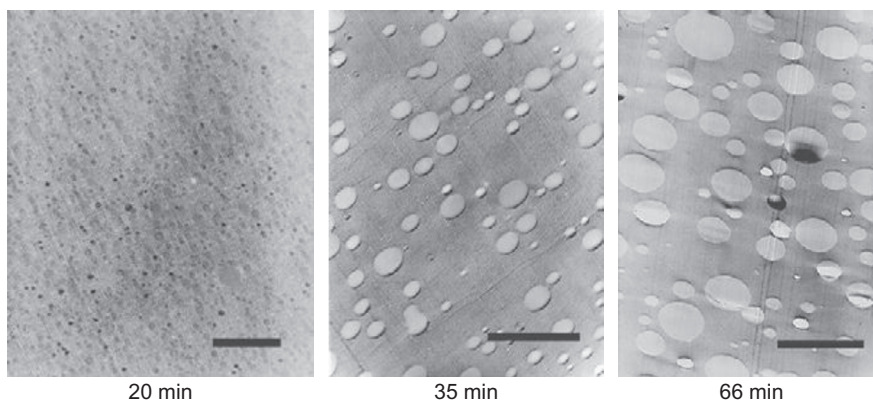|		
20 min	35 min	66 min

FIGURE 2.4

PS/DGEBA-MDEA 60/40 polymerized at 177 °C. Morphology of the blend at different reaction times (the epoxy-amine drops appear in light gray) [63].

2.6 PREPARATION OF NANOSTRUCTURED THERMOPLASTIC/THERMOSET BLENDS

The preparation of nanostructured polymer blends for immiscible polymers, with a phase size of less than 100 nm, is very challenging using normal processing methods currently available. Typically, blends of this type are prepared by one of three methods: solution casting, melt extrusion, or reactive blending [7]. Very recently, nanostructured blends have been produced from block copolymers by using conventional melt processing [64].

Improvement of the high-temperature properties of thermoplastics by blending it with a high-melting-temperature polymer such as thermosets is problematic because such blends naturally tend to phase separation on the macroscopic scale. As a result of this, a significant improvement of thermal and mechanical properties such as toughness, stress at break or high-temperature creep resistance can be achieved only when the thermoset phase is continuous. The challenge is to make the thermoset phase continuous while keeping the thermoplastic as the major component.

2.6.1 MELT EXTRUSION

The most common industrial method [65] of making polymer blends is by mixing the molten polymers in a twin-screw extruder (essentially a complicated Archimedes screw). When two immiscible polymers are blended during melt extrusion, a stable morphology is reached in which one phase is mechanically dispersed inside the other. The size and shape of the dispersed phase depend on several processing parameters, including rheological and interfacial properties and the composition of the blend [50]. Melt blending can also use a single-screw extruder with special mixing head over the whole range of compositions [59].

2.6.2 HIGHER SHEAR PROCESSING

Shimizu et al. [51] described a simple mechanical method of obtaining a nanostructured polymer blend. It is a melt extrusion method processed under high shear flow. The method was based on the *in situ* phase behavior of polymer blends under a high shear flow field. Immiscible poly(*p*-phenylene sulfide)/polyamide blends, a thermoplastic/thermoset blend was found to show a miscible region under a flow field with a high shear rate above $1000 \, s^{-1}$ and this was enlarged by a higher shear rate of $3000 \, s^{-1}$. They developed the high-shear extruder HSE3000mini which can reach a maximum screw rotation speed of 3000 rpm. A specially designed feedback type screw ($L/D = 1.78$) was used to make the sample to circulate in the extruder during melt mixing. The sample feed at the top of the screw was back soon at the root of the screw through the feedback path. By using this new high-shear extruder with the capability of about 5 mL, PVDF and PA11 were directly melt-blended. They found that PA11 can be dispersed in the PVDF phase with a domain size of several tens of nanometers.

2.6.3 PHYSICAL BLENDING

In physical blending, the compatibilizing agent is chemically synthesized prior to the blending operation, and subsequently added to the blend components as a non-reactive component. Owing to its chemical and molecular characteristics, the added agent is able to locate at the interface, reducing the interfacial tension between the blend components (emulsification effect), control the coalescence and

improve the adhesion between the two phases [35]. This results in the quenching of non-equilibrium morphologies produced during intensive high-temperature mixing of blend components. The major difficulty here is to achieve sub-micrometer structure by mechanical mixing, and to preserve the optimized morphology during the processing stage. The interface in immiscible polymer blends during mixing is never at equilibrium due to continuous deformation, break-up, and coalescence of the phases, caused by external flow in the mixer. The extent of deformation is greatest in the early stage of mixing, less than 2 min, where the interfacial area increases by approximately 1000 times [66]. In addition to the change in interfacial area by deformation, convection due to flow may contribute to the kinetics and the extent of interfacial reaction.

2.6.4 **REACTIVE BLENDING**

In recent times plastics have been toughened by reactive blending method [58]. For example, polyamide, PP and PE terephthalate are toughened using maleic anhydride grafted ABS. The same technique was followed for toughening polybutylene terephthalate with maleic anhydride grafted ethylene-propylene copolymer. Reactive blending was applied to compatibilization of maleic anhydride grafted styrene-ethylene-butadiene terblock copolymer with a polyamide/PC blend system. In the above examples, the interesting feature is that the toughness improvement/compatibilization could be achieved throughout the whole composition range of the blends [58].

Reactive blending, utilizing the concept of *in situ* polymerization, and graft and block copolymerization lead to the creation of nanostructure blends [8]. Although numerous chemical reactions are encountered in reactive processing, it is possible to distinguish major classes such as bulk polymerization, reactive compatibilization, controlled degradation, coupling, grafting, and functionalization. All these types of reactions can be classified under reactive processing. In reactive compatibilization, copolymers can be formed *in situ* through covalent or ironic bonding during melt blending. In this kind of reactive compatibilization, generally one phase contains reactive groups inherent in the polymer, while the other has no inherent functionality. Reactive groups can be incorporated into the second phase by adding to it a functionalized polymer, which is miscible. In some cases, both polymers have to be functionalized [35]. Pernot et al. [5] showed a general method to obtain stable co-continuous polymer materials with finely dispersed co-continuous morphologies structured at the nanometre scale, and demonstrated that, for the PE and polyamide pair, that the formed blend can exhibit a remarkable combination of properties. This method uses self-assembling and structuring properties of block copolymers which are linear macromolecules consisting of two or more monomer sequences covalently linked together. In a striking analogy with surfactant molecules and microemulsions, A-B block copolymers with carefully controlled molecular weight and composition are expected to self-assemble when mixed with the homopolymers A and B to form, under favorable conditions, thermodynamically stable co-continuous structures at the nanometre scale. Although many polymer pairs, such as PE and polyamide, are very difficult or just impossible to synthesize into linear block copolymers, Pernot et al. [5] demonstrated that reactive blending impart microscopic organization and thermodynamic stability of the blend by introducing poly-dispersity and randomness in order to produce crystalline materials, which are structured on the scale of tens of nanometres. In this process, two polymers carrying complementary reactive groups are mixed together and react at high temperature. The backbone polymers, B, carry reactive groups randomly distributed along their length, whereas the A chains, the grafts, are functionalized at one end only. The

challenge is to achieve a thermodynamic self-assembly of random graft copolymers formed *in situ* without expulsion and phase separation of unreacted chains. The poly-dispersity of the backbone and of the grafts, as well as the randomness in graft-attachment positions paradoxically helps to stabilize disordered co-continuous structures. Indeed, it enables local fluctuations of the interface curvature, and facilitates the incorporation of homopolymer in blends. This is a unique polymeric effect. In low molecular weight surfactant systems, co-surfactants with slightly different surfactant molecules are usually introduced to increase the interface flexibility and thereby stabilize a microemulsion phase. Here, a well-adapted molecular weight distribution and inherent molecular disorder may naturally yield a co-surfactant-like effect.

Two types of copolymer formation have been described; these are block and graft copolymer formation. Both can be achieved by a coupling reaction between polymer-bound functional groups to stabilize morphology and enhance adhesion between immiscible polymers. Copolymer formation must occur during typical processing time in less than 5 min [66]. This means that coupling reaction should be fast and the interface needs to be covered with an amount of reactively formed copolymer sufficient to make a compatible blend and/or to increase adhesion within the processing time. It is well known that block copolymer and solvent additives can shift the phase boundary of polymer blends and this idea is a common strategy for "compatibilizing" polymer blends. The usual goal for forming these mixtures is to achieve greater miscibility and reduced interfacial tension so that dispersion of one polymer within another is accomplished more readily than without the additive [43].

In commercial reactive blends, rather than diblock copolymers, graft copolymers are typically formed by the reaction between coupling agents with functional groups randomly distributed along a chain and end functional polymers like polyamides or polyester [66]. Functional groups for commercial blends must be fast enough and must not be sensitive to water and the bond must be stable at high temperature. As a result of steric hindrance due to the polymer chain, coupling with the mid-functional polymer is slower than with the end-functional polymer even in a homogeneous melt.

2.7 INTRODUCTION OF NANOPARTICLES

Presently, it is well established that introduction of a filler into polymer blends leads to the changes in thermodynamic interaction parameter between two polymeric components. Depending on the nature of interaction between polymeric components and filler surface, may either increase or decrease. Simultaneously, the shape of phase diagrams and the temperatures of phase separation are also changed. The introduction of filler diminishes the rates of the phase separation and initiates some other effects [67]. It was established that introduction of a filler increases the thermodynamic stability of the mixture (effect of compatibilization) and changes the compositions of separated phases. The observed effects were explained by the specific interaction of the mixture components with the active groups at the interface with solid and by the surface segregation of one of the components. Carbon black also referred to as nanofiller was incorporated essentially to produce polymers with antistatic properties (conductivity) by taking advantage of an optimized state of aggregation and distribution of the filler through the concept of double percolation [46].

Nesterov et al. [68] demonstrated that the studies on the kinetics of phase separation show that the phase separation rate of filled mixtures is much lower than that of unfilled mixtures at temperatures equidistant from the corresponding cloud-point curves. It is established that the phase separation of mixtures occurs in two stages. This can be associated with the structure rearrangement of the phases formed during phase separation. The differences in phase separation of filled and unfilled mixtures can be explained by the specific interactions between filler and one of the components of a binary polymer mixture. The investigation showed that the PVA/PMMA mixtures are compatible and separate on heating exhibiting lower critical solution temperature (LCST) behavior, and the addition of mineral filler decreases the phase separation temperature. With the difference in the energy of selective interaction between the polymers and the filler becoming smaller, the phase separation temperature decreases to a lesser extent. The rate of phase separation slows down when mineral filler is added, and the molecular weight distribution of a selectively adsorbed component of the mixture does not change. The change of compatibility is determined by the asymmetry of pair interactions in the system. Nanofillers used today include spherical and aggregated silicas, nanoclays, micas, carbon nanotubes, POSS and they vary by their shape factor (spheres, platelets, fibers), their surface energy and their ability to more or less disagglomerate or exfoliate depending on the mixing conditions and on the surface treatments applied [46,69].

Ginzburg [70] proposed a theory to predict how nanoparticles interacting symmetrically with the polymers can influence the behavior of the blend. Depending on the particle radius and the polymer chain length, the presence of nanoparticles can either promote or hinder mixing of the polymers. Actually, the nanoparticles influence the shape and the location of the spinodal curve according to their size. If the radius of the nanoparticles is smaller than the radius of gyration of the macromolecule, the addition of the solid stabilizes the homogeneous phase because they reduce the number of unfavorable polymer/polymer interaction and therefore decreases the enthalpy of the blend. As the particle size becomes much larger than the polymer radius of gyration, the particle-rich phase segregates from the blend even at very low concentration. Then, nanoparticles can facilitate polymer blend miscibility provided that their sizes are lower than the polymer radius gyration, typically approximately 15 nm. Furthermore, the high entropy of such small particles can also assist the free energy reduction and then the stability of the homogeneous phase.

As stated earlier, due to entropic effect disfavoring miscibility, polymers are most often immiscible. Although, more rarely, some polymer pairs may exhibit partial miscibility either by cooling, for the systems with LCST, or by heating, for the systems with upper critical solution temperature [46]. Generally speaking, a change in the cloud point curves and phase compositions are reported due to the presence of nanofillers. It is proposed that the differences in phase separation of filled and unfilled mixtures can be linked to specific interactions and to preferential adsorption existing between the filler and one of the components of the blend. Fenouillot et al. [46] proposed that a border layer is formed whose composition differs from the bulk leading to a system consists in regions with different polymer conformations and concentrations characterized by their own phase behavior, different from that on the unfilled system. Upon phase separation, four phases will be formed: two phases at the interface and two in the bulk. This situation is valid only in the case of asymmetric interactions with the surface. Another reason for changing the shape and position of the phase diagram is the possible selective adsorption of low- (or high-) molecular-weight fractions between the surface filler and the bulk which modifies the local molecular weight distribution.

2.8 MORPHOLOGY DEVELOPMENT

The morphology of a two phase structure formed in the mixing of two immiscible polymers is strongly dependent on the applied shear, volume, viscosity ratio, and the magnitude of the interfacial tension between the components [71]. The morphology of a polymer bend at a given composition is determined by the blending history and the interface properties [72]. The behaviors of polymer bends such as phase separation, miscibility, adhesion, and interface phenomena can only be understood if nanometer-scale structures and morphologies of block copolymers and their blends are known. Most common method for investigating bulk nanometer-scale structures and morphologies of polymer bulks is TEM, while scanning electron microscopy (SEM), electric force microscopy (EFM), and atomic force microscopy (AFM) have been used to investigate polymer surfaces. Small-angle X-ray scattering has also been used to study micro-phase structures of block copolymers.

Figure 2.5a-c were used by Shimizu et al. [51] to show that the miscibility between PVDF and PA11 was improved by the high-shear processing to form a partially miscible state with the nanosize dispersion. Figure 2.5a shows a typical TEM image for the high-shear-processed PVDF/PA11 blend which was processed by the high-shear extruder at 230 °C for 4 min (screw rotation speed of 1200 rpm). In this figure, PA 11 is observed as a dark phase and PVDF is observed as a white phase because PA11 is more readily stained than PVDF. As shown in Figure 2.5a, the nano-sized PA11 domains (the dark phase) are estimated to be 20-100 nm, and they are dispersed precisely in the PVDF phase. Figure 2.5b and c shows the EDX spectra of the respective parts designated in Figure 2.5a, the horizontal axis represents the energy corresponding to the specific X-ray emitted and the vertical axis represents intensity counts of the X-ray. Figure 2.5b and c suggests that the PA11 chains are mixed with the PVDF chains in the nano-spots with a diameter of 10 nm. The TEM-EDX results suggest that both the PVDF and PA11 chains mixed with each other after the high-shear processing.

PC/ABS blends are thermoplastic/thermoset blends whose morphology was described as complex [59]. The morphology depends on the type of ABS, processing machinery, processing parameters like operating speed and temperature, viscosity ratio, and volume fraction. Morphology of PC/ABS blends also depends on: (i) interfacial interaction; (ii) degradation of PC; and (iii) differential shrinkage between constituents. Lack of interfacial interaction between PC and ABS is known to produce coarse morphology. In commercial processes, the interfacial interaction is improved by the addition of a compatibilizer/copolymer. The melt degraded fractions which leave behind pin holes and voids cause stress concentration sites when subjected to load. Shrinkage differences of polymer constituents causes inter laminar voids which can be avoided through a compatibilization process. SEM micrographs of PC/ABS blends with different weight fractions are shown in Figure 2.6. Irrespective of the composition, the micrographs of fractured surfaces show coarse dispersion and rough surfaces characteristic of brittle failure. The pin holes on fractured surfaces are due to PC deterioration. Figures 2.5 shows the TEM/EDS images of PVDF/PA11 processed [51] at 80/20 blend processed at 230 °C for 4 min (screw rotation speed of 1200 rpm) 80/20 blend processed at 230 °C for 4 min (screw rotation speed of 1200 rpm), while Figure 2.6 shows SEM micrographs of notched impact-fractured [52] specimens of PC/ABS blends: (a) P25 (33,500), (b) P35 (33,500), (c) P50 (33,500), (d) P65 (31,000), (e) P75 (33,500), and (f) P90 (33,500).

Figure 2.7 shows the AFM and EFM characterization of spin-casting films formed from blends of poly (2-methoxy-5-(2′-ethylhexyloxy)/1,4-phenylenevinylene) MEH-PPV conjugated polymer and thermoplastic polyurethane TPU at different concentrations [73].
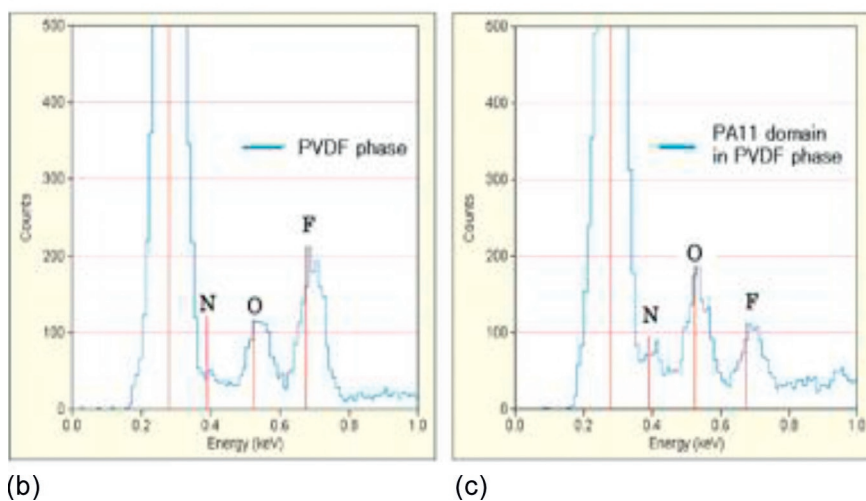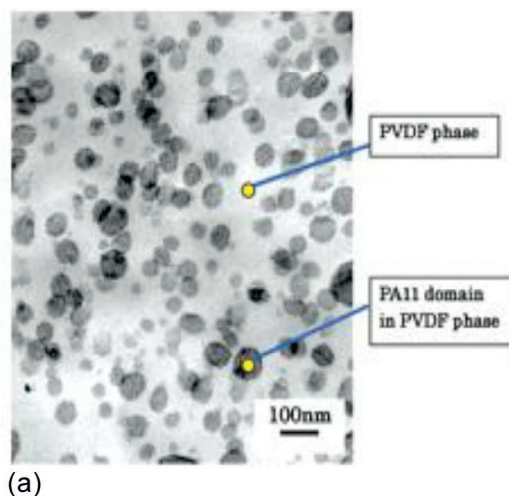
FIGURE 2.5

TEM image (a) and TEM-EDX spectra (b, c) of PVDF/PA11 80/20 blend processed at 230 °C for 4 min (screw rotation speed of 1200 rpm) [51].

Luo et al. [74] described what they called bricks and mortar morphology in a thermoplastic and thermoset blend in the process of development of thermally mendable polymeric materials through an epoxy/poly(caprolactone) (PCL) phase-separated blend. The initially miscible blend composed of 15.5 wt% PCL undergoes polymerization-induced phase separation during cross-linking of the epoxy, yielding a "bricks and mortar" morphology wherein the epoxy phase exists as interconnected spheres (bricks) interpenetrated with a percolating PCL matrix (mortar). The fully cured material is stiff, strong, and durable.
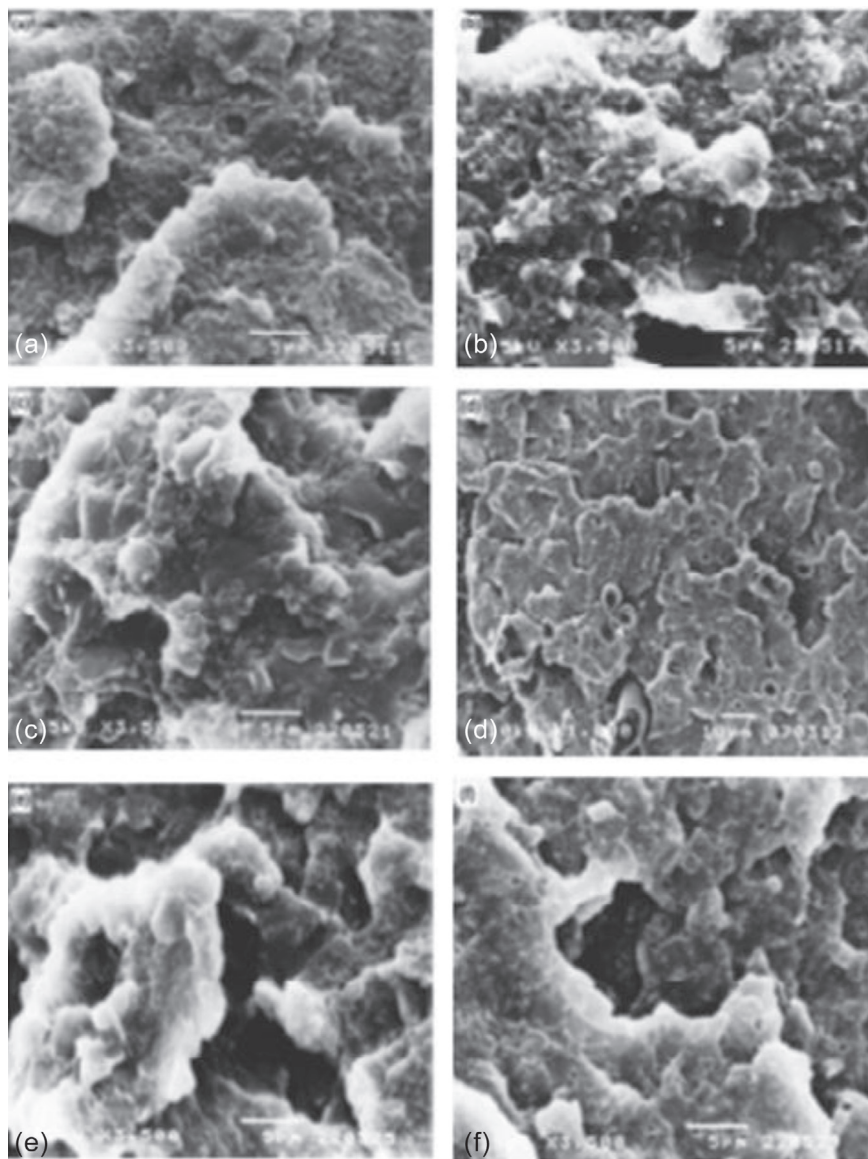
FIGURE 2.6

SEM micrographs of notched impact-fractured specimens of PC/ABS blends: (a) P25 (33,500), (b) P35 (33,500), (c) P50 (33,500), (d) P65 (31,000), (e) P75 (33,500), and (f) P90 (33,500) [58].

Bhardwaj and Mohanty [8] proposed and demonstrated a new industrially relevant methodology to develop a polylactide (PLA)-based nano blend having outstanding stiffness-toughness balance. In this approach, a hydroxyl functional hyper branched polymer (HBP) was *in situ* cross-linked with a polyanhydride (PA) in the PLA matrix during melt processing. There was formation of new HBP-based cross-linked particles in the PLA matrix. TEM and AFM revealed the sea-island morphology of
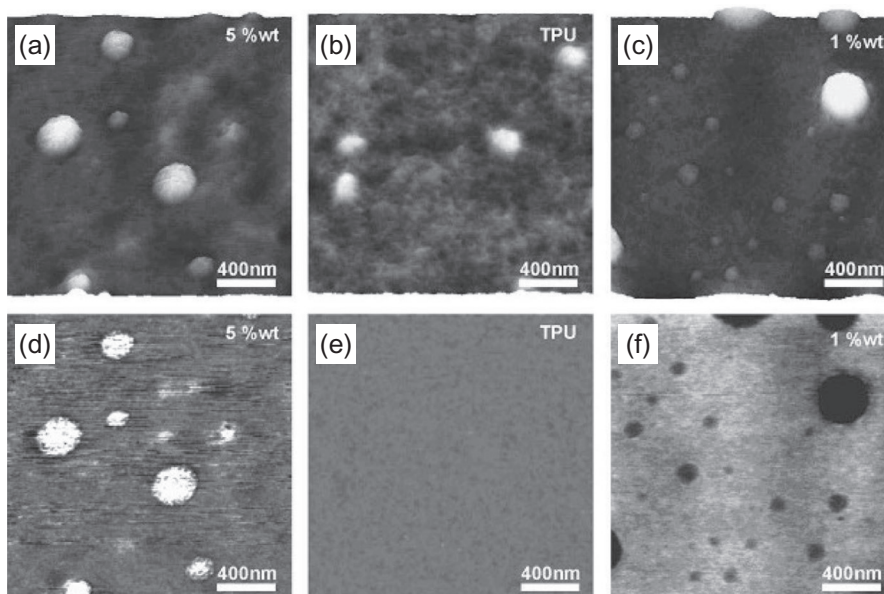
FIGURE 2.7

Topographic AFM images of the blended spin-casting film at concentration of (a) 5.0wt%; (b) pure TPU; (c) the blended spin-casting film at concentration of 1.0wt%; (d) and (e) show phase contrast-AFM images of the same regions of (a) and (b), respectively; (f) shows a frequency shift EFM image of the same region of (c) with the tip biased at −5.0V. The scale bars at the bottom right of all images show their lateral dimensions. The gray scale (z-axis scale) is 15nm for images (a)-(c), 10° for images (d) and (e) and 10Hz for image (f) [73].

PLA-cross-linked HBP blend. The domain size of cross-linked HBP particles in the PLA matrix was less than 100nm as obtained from TEM. The presence of cross-linked HBP in the PLA matrix exhibited 570% and 847% improvement in the toughness and elongation at break, respectively, as compared to unmodified PLA. The increase in the ductility of modified PLA was related to stress whitening and multiple crazing initiated in the presence of cross-linked HBP particles. Formation of a networked interface as revealed by rheological data was associated with enhanced compatibility of the PLA-cross-linked HBP blend as compared to the PLA-HBP blend. The cross-linking reaction of HBP with PA was confirmed with the help of Fourier transform infrared spectroscopy and low-temperature dynamical mechanical thermal analysis (DMTA).

Teng and Chang [75] reported a work whereby a homogeneous blend of amine-terminated acrylonitrile-co-butadiene rubber and the liquid DGEBA were obtained by slow curing at 15°C so that the diffusion of the liquid rubber to form a separated phase was limited due to high viscosity. Essentially, all the studies on thermoplastic/thermoset blends previously reported involve a homogeneous, pre-cured mixture consisting of the thermoplastic, the epoxy monomer and the curing reagent [75,76]. As the resin cures, the molecular weight increase causes a decrease in the configurational entropy of mixing. This is thermodynamically unfavorable for a miscible system owing to the increase in the free energy of mixing. Other than from a purely thermodynamic viewpoint, kinetic factors are also important in determining the final morphological properties of a cured resin [75].

2.9 PROPERTIES

Fine and Pascault [77] compatibilized thermoplastic/thermoset blends by block copolymers. The thermoplastic is poly(phenylene ether) and the thermoset precursors are a liquid epoxy, DGEBA and an aromatic diamine (4,4-methylene bis-3-chloro 2,6 diethylaniline, MCDEA). The triblock poly(styrene-b-butadiene-b-methyl methacrylate), SBM was chosen because PS blocks interact very favorably with PPE, PMMA blocks remain miscible with the thermoset during the whole curing process, and also PB mid blocks are expected to cover the interface. Morphologies of blends were observed by transmission electron microscopy and phase composition evaluated by DMTA. They observed that the strong repulsion between the thermoplastic PPE and the PMMA blocks governs the organization of the blend before reaction. As a consequence, the block copolymer is always at the interface between the matrix and nodules during the curing process. They demonstrated that the number of SBM micelles and their degree of dispersion is the main parameter controlling the mechanical properties. But in some cases SBM can be also be found inside the epoxy nodules depending on the length and percentage of the blocks. The polymerization only induces a purification of the matrix. The block copolymers can have some effects on the reaction-induced morphology of the blend, the stronger effect being observed in the region of phase inversion. The crack propagation resistance can be greatly enhanced by the presence of the triblock copolymer, and it was demonstrated that the number of SBM micelles and their degree of dispersion inside the PPE matrix is the main parameter. These blends based on PPE are easy to transform and they have also good fire resistance properties and a low dielectric constant.

Wu et al. [78] fabricated a photovoltaic (PV) device based on the polymer blends of poly(3-hexylthiophene) (P3HT)/PMMA and inorganic TiO_2 nano-rod bulk hetero junction. The optimized PV device with 1.6 wt% PMMA concentration has a power conversion efficiency of 0.65% under simulated AM1.5 illumination (100 mW/cm^2), which is 38% more efficient than the device without the incorporation of PMMA. Furthermore, the PMMA-included device gives a short-circuit current density of 2.57 mA/cm^2, an open-circuit voltage of 0.53 V and a fill factor of 0.48. They reported that having optimal PMMA concentration in the PV devices helps to smoothen the surface of the hybrid thin film, broaden the absorption spectrum, improve the electrical conductivity and thus improve the performance of PV devices by more than 38% efficiency as compared with the device without the incorporation of PMMA. Yang et al. [79] studied the morphologies of polymer blends based on MEH-PPV by using transmission electron microscopy. They reported that the phase separation in the blend films results in nano-scale network structure by controlling the preparation conditions, leading to nanostructured self-assembled polymer blends, with enhanced electronic and optical properties. This is actually interesting because polymer blends usually result in macro-phase separation, which limits the efficiency of charge separation and power conversion in a PV device [80]. The mechanical properties of polymer blends nanostructure have been largely studied, as shown in Table 2.1 and Figure 2.8.

Frenot and Chronakis [81] described a novel fabrication process called electrostatic spinning, or "electrospinning," which is capable of producing polymer fibers in the nanometer diameter range. It can be utilized to assemble fibrous polymer mats composed of fiber diameters ranging from several microns down to fibers with diameter lower than 100 nm. This electrostatic processing method uses a high-voltage electric field to form solid fibers from a polymeric fluid stream either from solution or melt extrusion delivered through a millimeter-scale nozzle. Nanofibers are the ultra-fine solid fibers notable for their very small diameters (lower than 100 nm), their large surface area per unit mass and small pore size. Due to the inherent properties of the electrospinning process, which can control the deposition

Table 2.1 Mechanical Properties of Polymer Blends Nanostructure

Composition	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (kJ/m²)	Elongation at Break Point (%)	References
PP/PA6/3T/5M	46.76 ± 0.56	0.493	76.32 ± 0.80	1.21	–	36.84 ± 0.29	[57]
PA6/PP/5E/4TC	47	2.25	95	2.02	–	6.7	[61]
PP/EOC/ PP-*g*-MA/clay	20.1 ± 0.4	1.17	–	1.15	4.3 ± 1.6	550 ± 105	[53]
PA6/PP/4S-MMT	47	2.05	69.1	2.25	4.98	3.3	[81]
PET/PP/1 wt% clay	28 ± 5.3	–	–	–		–	[48]

4 wt% organoclay (4TC), 3 wt% TiO$_2$ (3T), 5 wt% maleated ethylene-propylene (5E) and 4 wt% stearylamine modified organoclay (4S).
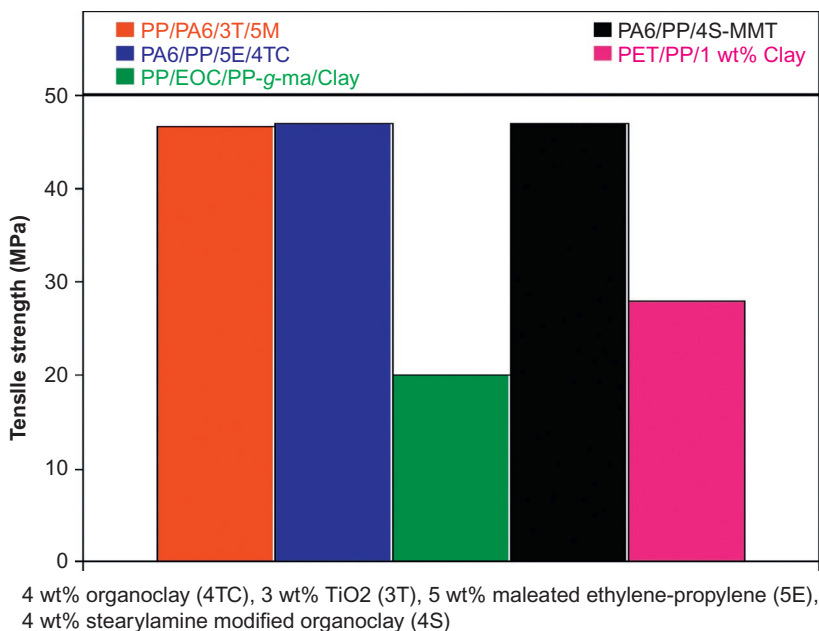
FIGURE 2.8

Tensile strength of different polymer blends nanostructure [47,52,57,60,82].

of polymer fibers onto a target substrate, nanofibers with complex, and seamless three-dimensional shapes could be formed. Construction of nanoscale composite fibers by electrospinning from a mixture of rigid rod polymers and flexible polymers is also feasible. The electrospun nanofibers can even be aligned to construct unique functional nanostructures, such as nanotubes and nanowires. Furthermore, depending on the specific polymer being used, a wide range of fabric properties, such as strength, weight, and porosity, surface functionality can be achieved. This novel fiber spinning technique also

provides the capacity to lace together a variety of types of polymers, fibers, and particles to produce ultrathin layers. Small insoluble particles can be added to the polymer solution and encapsulated in the dry nanofibers. Soluble drugs or bacterial agents can be added and electrospun into non-woven mats.

Balakrishnana et al. [58] described the improvement of the properties of a thermoplastic, PC by blending with ABS, a thermoset. PC is used in specialty applications due to its high toughness, higher continuous working temperature, high modulus, and transparency. The drawbacks of PC are high melt viscosity, which makes it difficult to be processed, and notch sensitivity. The disadvantages of PC can be overcome by blending with various thermoplastics-thermoplastics elastomers, of which ABS is the most popular. The addition of ABS minimizes the drawbacks of PC, retains the other superior mechanical properties and also generates other useful properties, such as glossiness and low-temperature toughness. PC/ABS alloys are the largest selling commercial polymer alloys in the world and are replacing polyester and nylon-based alloys in engineering applications [58].

Polysulfone PSU is a typical amorphous polyarylether and it shows high heat resistance, nice dimensional stability, and good mechanical properties. However, it has low stress crack resistance and high melt viscosity, which could be overcome by blending with Polyamine PA, a partially crystalline polymer [83].

2.10 CONCLUSION AND RECOMMENDATION

Nanostructured polymer blends offer specific electronic, mechanical, and optical properties, which make them useful for small and large scale industrial applications and scientific solutions because of enhanced thermos-mechanical properties, optical transparency, and toughness in comparison to conventional polymer blends. These properties are as a result of the presence of particles with structures that have dimensions in nanometer range with inherently high surface-area-volume ratio. Thermoplastics and thermosets form a highly incompatible blend due to their large differences in polarity and high interfacial tensions. However, when thermoplastics are blended with thermosets, the blends can reduce costs and improve the processability of thermoplastics leading to improvement of the mechanical, thermal, and chemical properties of thermoplastics and increasing the impact strength, adhesion, printability and paintability characteristics of thermosets. The majority of thermoplastics/thermosets blends are immiscible as a result of the large unfavorable enthalpy of mixing. This causes phase separated morphology resulting to deterioration in mechanical properties. Improvement of the high-temperature properties of thermoplastics by blending it with a high-melting-temperature polymer, such as a thermoset, is problematic because such blends naturally tend to phase separation on the macroscopic scale. As a result of this, a significant improvement of thermal and mechanical properties such as toughness, stress at break or high-temperature creep resistance can be achieved only when the thermoset phase is continuous. The challenge is to make the thermoset phase continuous while keeping the thermoplastic as the major component. The morphology of a two phase structure formed in the mixing of two immiscible polymers is strongly dependent on the applied shear, volume, viscosity ratio, and the magnitude of the interfacial tension between the components. Therefore, it becomes mandatory to control the phase behavior and morphology if these immiscible blends are to be converted into polymeric products for useful and practical application purposes. The challenge is to reduce phase size and improve interfacial adhesion of the blends. The traditional method for manipulating the interface properties of polymer blends is adding some copolymers as compatibilizers. In general, the added copolymers are compatible

with the phases, thereby segregating preferentially at the interface and ensuring strong interfacial adhesion. Addition of nanoparticles can reduce interfacial tension and improve miscibility between polymers and thus have a significant effect on phase behavior of polymer blends. However, the effect of nanoparticles on the miscibility of polymer blends depends greatly on the interactions among particles and polymers, which influences the location of nanoparticles in the phase-separated blends.

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