

POLYMER BLENDS

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27.1 INTRODUCTION

The modification of already existing polymers is more economically viable than the development of new monomers for the production of new types of polymers. High-value-added materials can be obtained either by new polymerization methods or by alloying or blending, and reinforcing existing polymer materials. Polymer modification processes based on simple mechanical mixtures of two or more polymers originated a new class of materials called *polymer blends*. A polymer blend, analogous to metal alloys, is the mixture of at least two different polymers to create a new type of material with different physical properties. The first polymer blend was patented in 1846 by Parkes [1]. This blend of natural rubber with gutta-percha resulted in a partially crosslinked material whose modulus was controllable by the composition of each isomer. The performance of polymer blends depends on the properties of each polymer in the blend, their content, and morphology. The cost of the blend depends on the material, compounding method, and blend morphology, which can be tailored for a specific application. Most blends have been developed for the improvement of a specific property such as impact strength, or extending the performance of an engineering resin, improving the processability or recycling facility, etc.

Polymer blends can be classified into the following categories:

1. *Immiscible Polymer Blends*. These blends have large-size domains of dispersed phase and poor adhesion between them. If the blend is formed by two polymers, two glass transition temperatures will be observed.
2. *Miscible Polymer Blends*. These are homogeneous blends with a single-phase structure. In this case, one glass transition temperature will be observed.
3. *Compatible Polymer Blends*. These are immiscible polymer blends that exhibit macroscopically uniform physical properties caused by sufficiently strong interface interactions between the polymer blend components.
4. *Compatibilized Polymer Blends*. Immiscible blends in which the microstructure and physical properties can be stabilized by adding surface-active species called *compatibilizers*. These compatibilizers will influence various morphological processes, such as deformation, breakup, and coalescence of droplets.

27.2 MISCIBILITY IN POLYMER BLENDS

Miscibility is similar to the thermodynamic solubility, that is, two or more polymers are miscible in each other if the free energy of mixing is negative. This is a function of the structural characteristics of the polymers, such as molecular weight, molecular weight distribution, copolymer composition, as well as of temperature, pressure and blend composition. Polymer blends can exhibit miscibility or phase separation and various levels of mixing in between the extremes. The most important factor leading to miscibility in low-molecular-weight materials is the combinatorial entropy contribution, which is very large compared to high-molecular-weight polymers. This contribution is the reason solvent–solvent mixtures offer a much broader range of miscibility than polymer–solvent combinations. The range

of miscible combinations involving polymer–polymer mixtures is even much smaller.

Miscibility in polymer blends is not a requirement; however, interfacial adhesion between the polymer components is highly desirable for enhancing specific properties of the blend.

One of the most important relationships that governs the behavior of dissimilar components is given by the change of free energy of mixing (ΔG_m), given by:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (27.1)$$

where ΔG_m is the free energy of mixing; ΔH_m , the enthalpy of mixing or heat of mixing; T , the absolute temperature; and ΔS_m , the entropy of mixing.

If two polymers are mixed, the most frequent result is a system that exhibits complete phase separation due to the repulsive interaction between the components (i.e., the chemical incompatibility between the polymers). A necessary condition for miscibility to occur is that ΔG_m must be negative ($\Delta G_m < 0$). This is a necessary requirement, but not a sufficient one, as the following expression must also be satisfied in order to obtain a stable one-phase system. The expression that describes the criteria for phase stability of binary mixtures of composition φ at fixed temperature T and pressure P is [2]:

$$\left[\frac{\partial^2 \Delta G_m}{\partial \varphi^2} \right]_{T,P} > 0 \quad (27.2)$$

Figure 27.1 shows a schematic phase diagram for binary blends showing the relationship between free energy of mixing (ΔG_m) and blend composition (φ). For sample A, an immiscible system is obtained ($\Delta G_m > 0$), for sample B a fully miscible system is obtained in which $\Delta G_m < 0$, and C represents a partially miscible system that satisfies $\Delta G_m < 0$ for all compositions, but $\partial^2 \Delta G_m / \partial \varphi^2$ is lower than 0 at certain compositions, indicating that at these compositions the blend will be immiscible.

A miscible polymer blend is a polymer blend that is homogeneous down to the molecular level and associated with negative values of the free energy of mixing, and whose domain size is comparable to the dimensions of the macromolecular statistical segment. The value of $T\Delta S_m$ is always positive because there is an increase in entropy when mixing takes place. Therefore, the sign of ΔG_m always depends on the value of the enthalpy of mixing ΔH_m that can be negative or positive but very small.

Traditionally, the thermodynamics of polymer mixtures was developed in terms of a lattice model, with each monomer unit of the polymer chains occupying a single lattice site. The free energy of mixing of polymers in solution can be described by the Flory–Huggins equation:

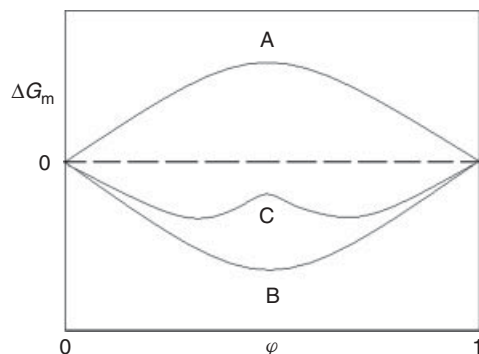


Figure 27.1 Schematic phase diagram for binary blends.

$$\Delta G_m = RTV \left[\frac{\varphi_A \ln \varphi_A}{V_A} + (1 - \varphi_A) \frac{\ln(1 - \varphi_A)}{V_B} + \chi_{AB}^* \varphi_A (1 - \varphi_A) \right] \quad (27.3)$$

where V is the total volume of the sample, R is the gas constant, T is the absolute temperature, φ_i is the volume fraction of each component, V_i is the molar volume of each specimen, and $\chi_{AB}^* = \chi_{AB}/V$ is the Flory binary interaction parameter.

The first two logarithmic terms give the combinatorial entropy of mixing, whereas the third term gives the enthalpy of mixing. For blends of polymers of high molecular weight, the volume (V_i) is quite large; thus, the combinatorial entropy is very small and the entropic stabilization is vanished. Hence, the negative value of ΔG_m required for mutual miscibility of the system will strongly depend on the value of the enthalpy of mixing or interaction contribution [$\chi_{AB}^* \varphi_A (1 - \varphi_A)$].

From this equation, it is clear why blends of high-molecular-weight polymers are different from small molecule mixtures. As most polymers have degrees of polymerization higher than 1000, the entropy of mixing is generally quite small. The interactions between two polymers are quite small compared to those between their small molecule monomers, and so the enthalpy of mixing will not depend on the molecular weight of the components. The enthalpy of mixing is positive for most mixtures and the rule of “like prefers like” always applies. Enthalpy will be negative and favorable to mixing if the two components interact through specific interactions, such as charge transfer or hydrogen bonding.

The entropy of mixing of small molecules can be so large that it overwhelms the positive mixing enthalpy and forces the components to mix under a wide range of temperature and compositions. This is why polyolefins,

such as polypropylene (PP) and polyethylene (PE), are immiscible under all conditions, whereas monomers of low molecular weight are miscible over a large range of conditions, which is simply due to the near absence of mixing entropy for the two high-molecular-weight polymers.

The enthalpy of mixing (ΔH_m) can be expressed in terms of solubility parameters:

$$\Delta H_m = V (\delta_A - \delta_B)^2 \varphi_A (1 - \varphi_A) \quad (27.4)$$

where δ_i are the Hildebrand solubility parameters.

Miscibility can be estimated by using solubility parameters, which are tabulated for many different polymers and solvents. Hildebrand solubility parameters have been used to predict the solubility of solvents in polymers [3]. If the exact solubility of a solvent is unknown, the Hildebrand parameters are useful to obtain an indication of the solubility and swelling behavior of the polymer under the load of a specific solvent. This parameter (δ) is a result of the following intermolecular forces: dispersion (δ_d), dipole–dipole (δ_p), and hydrogen bonding (δ_h). When a solvent and a polymer have a similar solubility parameter, the solubility of the solvent in the polymer is high. Table 27.1 lists typical values of solubility parameters for several polymers and solvents [4]. From Equations 27.1 and 27.4, it can be seen that the consumption of heat or enthalpy of mixing is small when the difference between solubility parameters is small. Thus, the entropy of mixing (a measure of chaos) from Equation 27.1, which is negative, will promote a favorable negative energy of mixing ($\Delta G_m < 0$). When the heat of mixing is high, only high temperatures will drive the entropy to a sufficient level that can compete with the heat of mixing. Therefore, solubility usually increases with temperature.

As a miscible polymer blend shows very low or even negative values of the Flory–Huggins interaction parameter

TABLE 27.1 Typical Values of Solubility Parameters for Solvents and Polymers

Solvent	δ_1 (cal/cm ³) ^{1/2}	Polymer	δ_2 (cal/cm ³) ^{1/2}
<i>n</i> -Hexane	7.24	Polyethylene	7.9
Carbon tetrachloride	8.58	Polystyrene	8.6
2-Butanone	9.04	Poly(methyl methacrylate)	9.1
Benzene	9.15	Poly(vinyl chloride)	9.5
Chloroform	9.24	Poly(ethylene terephthalate)	10.7
Acetone	9.71	Nylon 66	13.6
Methanol	14.5	Polyacrylonitrile	15.4

TABLE 27.2 Bond Energy and Relative Strength of Different Intermolecular Forces

Type of Interaction	Bond Energy (kJ/mol)	Relative Strength
Ionic attraction	850–1700	1000
Hydrogen bonding	50–170	100
Dipole–dipole interaction	2–8	10
van der Waals interaction	1	1

(χ_{AB}), some reports relate the miscibility of a polymer blend with polymer interactions in terms of intermolecular forces. Table 27.2 lists the bond energy and relative strength of different intermolecular forces. From this table, we can classify a miscible polymer blend with van der Waals interactions as one having weak interactions, and a miscible polymer blend with other types of interactions as one having strong interactions.

In polymer blends, different phase behaviors can be observed as shown in Figure 27.2. It is possible to calculate the compositions at which the blend will always separate into more than one phase (two-phase region), and also those compositions in which the blend may either form a single phase or will separate into several phases by different mechanisms, either in the metastable or in the spinodal regions. The binodals separate the miscible (one phase) and the metastable regions; the metastable region is

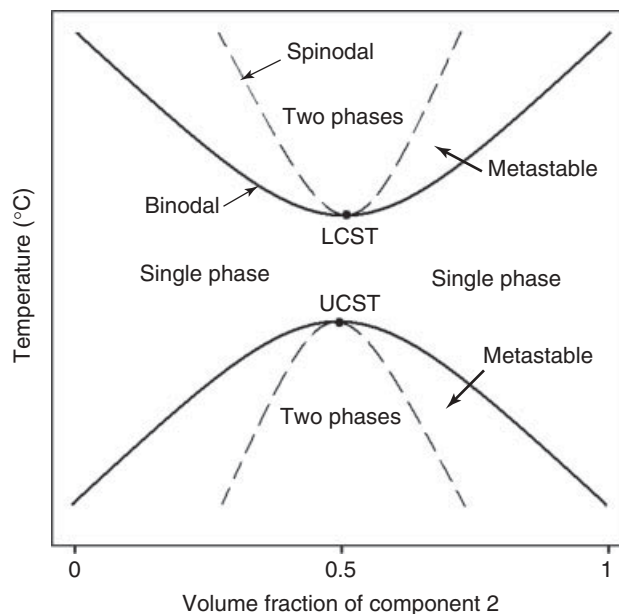


Figure 27.2 Phase diagram for binary blends showing the different phase regions and the upper and lower critical solution temperatures (UCST and LCST).

located between the binodal and spinodal curves and the two-phase separated region of immiscibility is bordered by the spinodal curve. This figure also shows the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST). Blends that have positive entropies and mixing heats (endothermic mixtures) usually tend to exhibit UCST, whereas blends that have negative values of entropies and enthalpies of mixing usually exhibit LCST. In other words, if the enthalpic interactions between polymer components are unfavorable, the blend will exhibit a UCST and it will be immiscible at lower temperatures, mainly due to weak interactions between them [5].

Phase separation takes place when a single-phase system suffers a change of temperature, pressure, or composition that forces it to enter either the metastable or the spinodal regions. Phase separation occurs by different mechanisms. When the system enters from a single-phase region (Fig. 27.2), uniform in composition, into the spinodal region of immiscibility where the mixture is unstable, phase separation occurs by a spontaneous and continuous process. This spontaneous process is attributed to a diffusional flux mechanism and is called *spinodal decomposition*. On the other hand, if the system enters from a single-phase region into the metastable region, phase separation occurs by a mechanism resembling crystallization: slow nucleation followed by growth of the phase-separated domains. In this mechanism, small fluctuations in composition form a nucleus and, once it is formed, it grows by a conventional

diffusion process [6]. This mechanism is called *nucleation and growth* (Fig. 27.3).

27.3 COMPATIBILITY IN POLYMER BLENDS

The main motivation for blending immiscible polymers is to create materials with combinations of properties superior to those of the individual components. However, immiscible polymer blends have the disadvantage that they are not thermodynamically stable. Therefore, postmixing processing, such as molding or annealing, can significantly affect blend morphology. Changes in morphology may reduce or eliminate the benefits achieved by blending. To address this challenge, the morphological stability of immiscible polymer blends is often improved by adding a compatibilizer agent, which preferentially locates at the polymer–polymer interface. The addition of such compatibilizers can lead to more stable, finer scale morphologies, by reducing the effective interfacial tension and slowing phase coarsening [7]. Figure 27.4 shows the effect of a block copolymer on the morphology of a PS/PE (polyethylene) blend in which a continuous reduction in the dispersed phase size is observed as the compatibilizer content is increased [8].

A compatibilized blend exhibits no gross symptoms of phase separation and has a desirable set of final properties. This implies at least some mixing of polymer segments on a microscopic scale and a certain thermodynamic

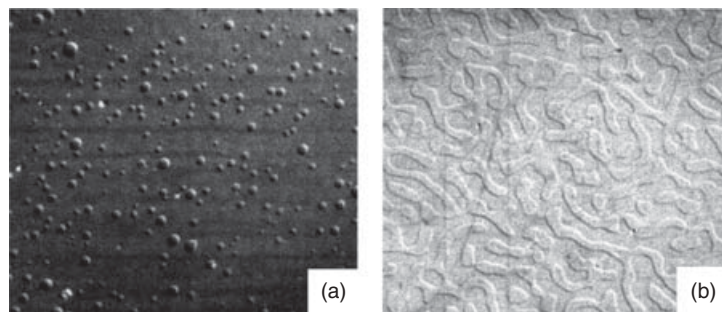


Figure 27.3 Blend images showing (a) nucleation and growth and (b) spinodal mechanisms.

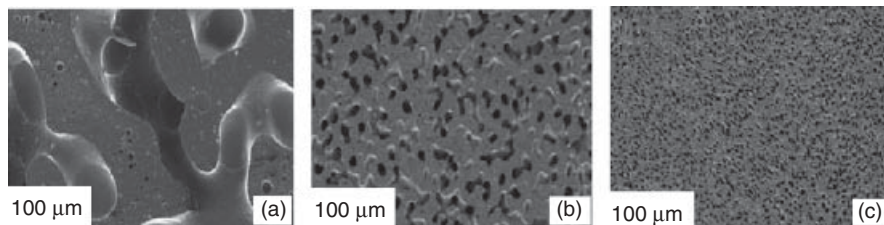


Figure 27.4 SEM micrographs of 50/50 PS/PE annealed polymer blends: (a) no block copolymer, (b) 0.3%, and (c) 1% of PS/PE block copolymer. *Source*: Reproduced with permission from Galloway JA, Jeon HK, Bell JR, Macosko CW. *Polymer* 2005;46(1):183–191 [8]. Copyright 2005 Elsevier.

compatibility that prevents demixing. It is important to realize that the highest degree of compatibility, in which complete miscibility has been reached ($\Delta G_m < 0$), does not always mean the best final properties. Most of the final mechanical properties require some amount of phase separation to produce the desired property [9].

The desired compatibilization can be obtained by different methods such as the addition of a third component (copolymer or functional polymer) or by inducing *in situ* chemical reactions (reactive blending) among blend components, leading to the modification of the polymer interfaces and tailoring the blend phase structure and the final properties. The final properties of a blend will be determined not only by the components properties but also by the phase morphology and the interface adhesion, both of which determine the stress transfer within the blend and its end-use applications.

The blend morphology is determined by the processing history to which the blend has been subjected. The processing history depends on several factors, such as type of mixer, rate of mixing, temperature, rheology of the blend components, and interfacial tension between phases.

Compatibilizers reduce the interfacial tension in the melt between blend components and retard the coalescence process via steric stabilization, leading to an extremely fine dispersion of one phase into the other one. Compatibilizers also improve stress transfer by increasing the adhesion between phases and stabilize the disperse phase against growth during further annealing.

One of the most studied approaches to compatibilize a blend is the addition of a third component, such as a block or graft copolymer. Copolymers that contain segments chemically identical to the blend components are frequently used because they enhance the miscibility between the copolymer segments and the corresponding blend component (Fig. 27.5).

To improve compatibilization, it is required that the copolymer preferentially locates at the blend interface.

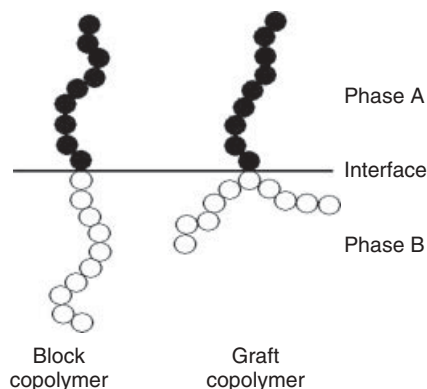


Figure 27.5 Schematic diagram showing interactions of block and graft copolymers through the interface.

The resistive force to diffusion increases with molecular weight; thus, copolymers with high molecular weight are preferred if long times are available during the mixing process and lower-molecular-weight copolymers must be used if available diffusion times are short. Although block copolymers are preferred over graft copolymers, they are often not commercially available and need to be tailor made for a particular blend [7, 9].

The addition of a functional or reactive polymer as a compatibilizer involves the use of a polymer chemically identical to one of the components of the blend, which has been functionalized with certain groups (e.g. polar groups) that have some affinity for the other blend component. This functional group may chemically react with the blend component or only interact with it by polar or ionic interactions.

The polymer may be modified with functional or reactive groups in a reactor or an extruder, via reactive extrusion. Polyolefin modified with maleic anhydride, acrylic acid, glycidyl methacrylate, acid groups neutralized with a metal cation (ionomer), itaconic acid, or anhydride or similar compounds have been widely reported as compatibilizers because these groups have the ability to form a chemical linkage or a polar or ionic interaction with polar polymers such as polyamides (PAs), polyesters, and others.

Another method for producing compatible blends is via reactive blending, which implies the *in situ* formation of copolymers during melt blending, with no need for addition of a separate compatibilizer. This method has found widely commercial application and can be carried out either in batch melt mixers or in continuous processing equipment using single- or twin-screw extruders. The use of twin-screw extruders in a continuous process allows better temperature control and can be designed to apply the shear stresses needed to improve blending and to remove the undesirable reaction byproducts by devolatilization.

27.4 TECHNIQUES FOR STUDYING BLEND MICROSTRUCTURE

Experimental study of blend miscibility or compatibility is more difficult for polymeric materials than for small molecules, because the heat of mixing (ΔH_m) is very small for polymers and is nearly impossible to measure directly. Because of the microscopic size of the dispersed phase, it is necessary to use special techniques to measure morphology on that very small scale. A brief sampling of the most important techniques used to study blend microstructure is offered below [6].

Measurement of the *glass transition temperature* of a blend is one of the most common ways to determine blend compatibility. Perhaps the most used criterion of polymer

compatibility is the detection of a single glass transition whose temperature is commonly intermediate between the glass transition temperatures corresponding to each one of the blend components. Thus, a general rule that has been applied is that if the blend displays two T_g s at or near the same temperatures of the blend components, then the blend is classified as incompatible. On the other hand, if the blend shows only a single transition temperature that is intermediate between those of the pure components, the blend is classified as compatible.

In addition, it is believed that a very broad, single glass transition in miscible polymer blends having little or very weak interactions is caused by the presence of concentration fluctuations that broaden the distribution of segmental relaxation times, which depend not only on blend composition but also on temperature. Further, it has been empirically observed that miscible polymer blends with large differences in T_g between the constituent components (ΔT_g) will give rise to failure of the time temperature superposition (TTS) principle. Glass transitions are determined with relative ease by thermal analysis using a differential scanning calorimeter (DSC), but this technique is limited to materials with significantly different T_g s and it cannot give information about the degree of compatibility.

Another technique commonly used is *light microscopy*, which is relatively simple and cheap, and requires non-complicated specimen preparation. The main disadvantage of this technique is the low resolution of light microscopes, which is limited by the wavelength of visible light. The visibility of blend phases can be enhanced by contrast techniques identifying the phases by staining or fluorescence. Samples made from two miscible or compatible polymers are optically clear, whereas those made from incompatible polymers are usually translucent or opaque. Some authors have reported that the critical domain size required for film transparency in a microheterogeneous blend is approximately 0.1 μm or 100 nm. The clarity observed in some blends is also affected by the refractive indices of the components or by the size of the dispersed phase, which could be smaller than the wavelength of visible light.

Scanning electron microscopy (SEM) can offer a good depth of field, good resolution, and easy specimen preparation. It can be used for immiscible polymer blends, where the phases are sufficiently large and can be easily debonded. Information on surface topography, size, and distribution of the dispersed phase and interfacial interaction between phases can be elucidated with this technique. Elemental analysis on the blend components can also be obtained if the SEM equipment includes an energy dispersion X-ray spectrometer (EDX).

Another microscopic technique is *transmission electron microscopy* (TEM), which offers higher resolution and

provides information on the fine structure of materials down to atomic or molecular levels and elemental analysis from small samples. A combination of the scanning and the transmission facilities can be obtained from a scanning transmission electron microscopy (STEM), which offers better image processing, much less beam damage of the analyzed samples, as well as accurate and high-quality diffraction patterns, which can be located on a specific area of the sample. It can be combined with other specific techniques such as back-scattered electrons or diffracted electrons to increase contrast.

This technique can be used to obtain structural information on very small scales approaching the molecular dimensions. It can be used to study surface morphology, internal structure, and crystallographic analysis. It can provide information about cocrystallization, very fine depression phases, or interfaces.

Spectroscopic techniques such as *FTIR*, *Raman*, or *NMR* can measure molecular interactions such as hydrogen bonds or specific chemical reactions. These techniques cannot give information about the phase inversion and are mostly nonquantitative.

Other techniques used with less frequency are *light*, *neutron* and *X-ray scattering*. In light scattering (Chapter 18), a laser beam is scattered on heterogeneities such as large molecules or molecular clusters. This technique can detect segregation of phases in solutions with temperature changes; thus, it can detect spinodal decompositions and can be used for the measurement of phase size and dispersion.

Neutron and X-ray scattering techniques use shorter wavelengths and require deuterated polymers for neutron and fluorinated polymers for X-ray scattering. The information obtained with these techniques is on the molecular scale and can reveal the arrangement of side groups, crystalline structure, and conformation of molecules.

27.5 PREPARATION OF POLYMER BLENDS

Preparation of polymer blends has been done by different types of machinery that includes internal mixers, such as single- or multishaft mixers, and extruders, such as single- or twin-screw extruders [9].

27.5.1 Mixers

Dry blends (powder blending) or blends of plasticized polymers are commonly prepared in a single-shaft mixer, such as ribbon blenders or paddle mixers.

Internal multishaft mixers that generate higher mechanical stress than single-shaft mixers whose shafts rotate at different speeds and whose charge is contained by a ram are used for melting and mixing of viscous masses. The

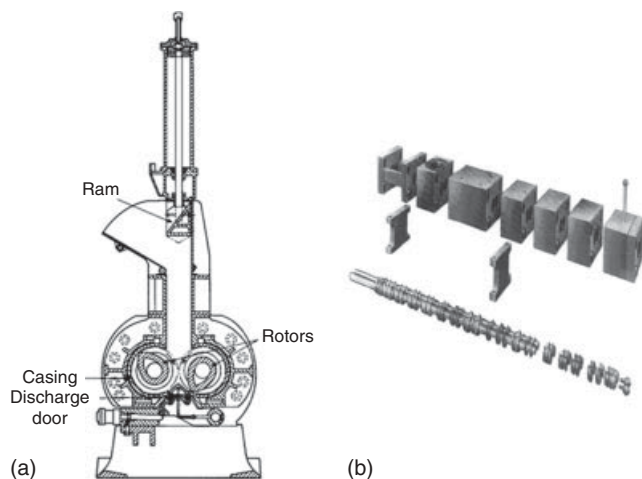


Figure 27.6 Devices used for polymer blend preparation: (a) internal multishaft batch mixer and (b) modular twin-screw extruder.

rotors are designed to cause flows to circulate through the mixer chamber. One of the most common internal mixers is the Banbury plasticizing batch mixer (Fig. 27.6a). This type of mixer is widely used for polymer blends such as rubbery polymer melts and blends of rubbers and plastics.

27.5.2 Extruders

Single-screw extruders have been widely used for blend preparation; however, they do not offer sufficiently high stress levels to improve mixing; thus, special designs of screws have been developed such as those with mixing heads or barrier zones that increase residence time and enhance blend mixing.

Twin-screw mixers (Fig. 27.6b) have demonstrated to be the most efficient devices to obtain higher mixing levels in polymer blends. An obvious advantage of these extruders over single-screw design is the additional distance along the periphery over which the melt is dragged in one revolution. These extruders are used for mixing, compounding, or reacting polymeric materials. They offer extreme versatility and allow their operation to be designed specifically for the blend formulation being processed. Twin-screw extruders (Chapter 23) are formed by two screws, side by side, placed within the extruder barrel; they could be either counter-rotating or corotating and intermeshing or nonintermeshing, depending on the way they rotate or the way they are matched together. The configurations of the screws may be varied using different types of mixing elements, such as forward conveying or reverse conveying, kneading blocks, vent stages, and other specific designs to achieve particular mixing characteristics. Corotating intermeshing units are

widely used for compounding materials where higher levels of mixing and high output rates are desirable.

The correct choice of compounder, operation conditions (rate, rpm, and temperature), feeding technique, and mixing elements of the compounder configuration has a significant effect on the quality of the resulting polymer blend. The capability of a compounder to generate shear stresses of sufficient magnitude to disrupt the stabilizing interfacial forces of the blend and the deformations field generated during plastication directly influences the dispersion mechanism.

27.6 FACTORS INFLUENCING THE MORPHOLOGY OF A POLYMER BLEND

Current commercial interest in blends is to a large degree focused on the dispersion and mixing characteristics of polymers in melt-compounding processing equipment, such as mixers and extruders. Controlling the factors that directly influence both control of interfacial modification and morphology, under melt processing conditions, have been widely studied over the years. The development and stability of morphology in multiphase polymer melts is a complex function of several factors, the most important being viscosity ratio, blend composition, applied shear stress, as well as elasticity and interfacial characteristics [9, 10].

A theory for the break up of individual droplets for Newtonian fluids has been developed and a relationship has been established between the capillary number (Ca), which is a ratio of shear to interfacial forces, and the viscosity ratio η_r ($\eta_r = \eta_d/\eta_m =$ dispersed phase viscosity/matrix phase viscosity), where G is shear rate, D is the diameter of the droplet, and γ is interfacial tension.

$$Ca = \frac{G\eta_m\Delta}{2\gamma} \quad (27.5)$$

The predicted drop size for a simple field is proportional to interfacial tension and inversely proportional to shear rate and matrix phase viscosity. Although Newtonian systems are relatively well understood, there are many limitations to this theory for predicting the morphology of a multiphase polymer system. Other difficulties in comparison with such ideal systems may include the complex shear fields applied in processing and the relatively high concentrations of the dispersed phase in most commercial polymer blends.

27.6.1 Viscosity Ratio

Viscosity ratio is the ratio between viscosity of the dispersed phase and the viscosity of the matrix. This

ratio has been shown to be one of the most important factors for controlling blend morphology. If the minor component of the blend has lower viscosity than the major component, that component will be finely and homogeneously dispersed. On the other hand, the minor component will be coarsely dispersed if it has higher viscosity than the major component. Some authors have found a linear relationship between the average diameter of the dispersed phase (minor phase) particles and the viscosity ratio [9, 10]. They have also reported that fine dispersion can be achieved if the viscosity of the minor phase is low and the value of the viscosity ratio is near unity. It has been demonstrated that as the viscosity ratio moves away from unity in either direction, the dispersed particles become larger. A higher matrix viscosity will stabilize the dispersed phase against capillarity instabilities. Thus, increasing the matrix viscosity would result in a more evenly distributed dispersion, mainly because it delays the breakup time and inhibits premature relaxation of the dispersed phase.

27.6.2 Blend Composition

For a given A–B blend, the composition of each component will define a specific region: (i) a region for which phase A is dispersed in matrix B, (ii) an intermediate region of phase inversion for which both A and B are cocontinuous, and (iii) a region in which the phase has been inverted in which now phase B is dispersed in matrix A (Fig. 27.7).

A variety of morphological structures can be obtained by varying the components, composition. Increasing the fraction of the dispersed phase results in an increase in particle size mainly owing to coalescence. As the minor phase concentration is increased, particle–particle interactions may

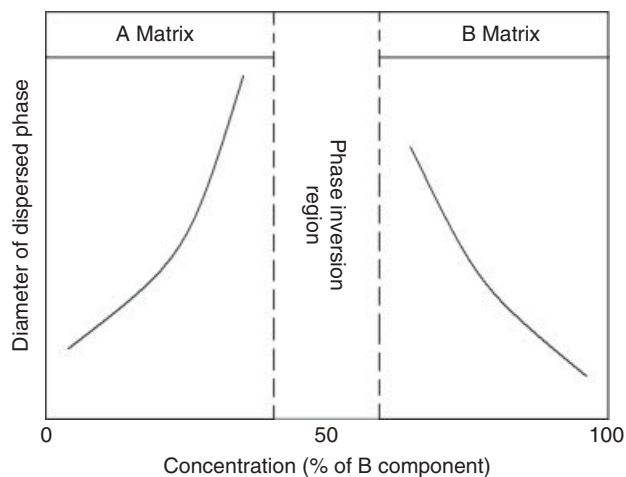


Figure 27.7 Variation of dispersed phase size in an A/B polymer blend as a function of component B concentration.

significantly increase and promote coalescence. It is clear that the extent of coalescence will depend to a large degree on the interfacial tension of the immiscible polymer components.

27.6.3 Shear Stress

As discussed earlier, from Equation 27.5, the phase size is inversely proportional to the applied shear stress. It has been demonstrated that shearing at high shear stress results in much finer and dispersed morphologies. The reported results have indicated that large variations in shear stress are required for this to predominate over the viscosity ratio in controlling the dispersed particle size. Increasing shear stress results in higher deformation of the dispersed phase and a fiberlike dispersed phase could even be formed. High shear rates may have a negative effect on the transient breakup process by suppressing capillary instability during flow.

27.6.4 Elasticity

The effect of elasticity in determining the morphology in a polymer blend remains one of the least understood aspects in this field. Some studies have shown that the elastic contribution to interfacial tension can result in a tendency for the phase of higher elasticity to encapsulate the one with lower elasticity, indicating that it is generally difficult to deform a highly elastic material. It has been reported that polymer blend morphology is not highly sensitive to changes in shear stress and shear rate when mixing in an internal mixer, and this was attributed to the viscoelastic nature of the dispersed droplets [11]. Although internal mixers are predominantly shear mixing devices, they can also induce elongational flow to the dispersed particles. The efficiency of elongational flow in droplet breakup has been demonstrated; however, the elastic component of molten polymers allows them to better retain their shapes after deformation.

27.6.5 Interfacial Characteristics

As described earlier, compatibilizers can enhance compatibility in a polymer blend by promoting physical or chemical interactions with blend components. If the compatibilizer locates at the interface, it will bind the two components together interlacing their phases. The main effect of interfacial modification on the morphology of an immiscible blend is a reduction on the particle size and a narrowing of the particle size distribution. This reduction in particle size is related with a decrease in the interfacial tension and a reduction in the coalescence process. Interfacial modification seems to be the dominant factor for controlling the dispersed phase size, and the dependence of this phase size

versus viscosity ratio is less pronounced for compatibilized systems in which an interfacial modification has occurred. The particle size on addition of an interfacial modifier is due to the reduction in interfacial tension as well as to reduced coalescence.

It has been demonstrated that when the rates of drop breakup and coalescence are in dynamic equilibrium, the particle size decreases as the applied stress increases and the interfacial tension between the phases decreases. For two particles to fuse in a bigger particle, they must first come into close proximity to each other by some flow process driven by a shear field, hydrodynamic interactions, gravity, or other forces. Once the two particles are in near contact, there is only a finite chance that coalescence of the particles will occur. Coalescence depends, among other variables, on the viscosity of the matrix phase that would allow sufficient time for drainage of the film between the dispersed phase domains. Several studies [12, 13] have shown that the dispersed phase particle size developed during processing can increase, decrease, or show a complex nonmonotonic behavior as the shear rate is increased, mainly because of the competing effects of increased particle–particle contacts versus decreased contact times. In addition, changes in polymer elasticity at high shear rates may also affect the dynamic equilibrium between coalescence and particle breakup.

27.7 PROPERTIES OF POLYMER BLENDS

27.7.1 Mechanical Properties

Mixing two or more polymers to produce blends or alloys is a well-established route to achieve a certain level of physical properties, without the need to synthesize specialized polymer systems. For example, an amorphous and brittle polymer, such as polystyrene, can increase its toughness when blending with polyethylene and a compatibilizer.

The goal of combining two or more polymers in a blend is to achieve a combination of favorable properties from each polymer. Figure 27.8 shows idealized expected property combinations from blending two polymers that are either miscible (center line), immiscible, and uncompatibilized (bottom line), or immiscible and compatibilized (top line). In the case of polymers that are miscible in all proportions, we can only obtain an average of their physical properties depending on the proportion of each polymer present. When two immiscible polymers are blended without compatibilization, one generally obtains physical properties worse than those of either individual polymer (antisynergic effect). Usually such a blend has poor structural integrity and poor heat stability because there is no mechanism for stabilizing a dispersion of one polymer in a

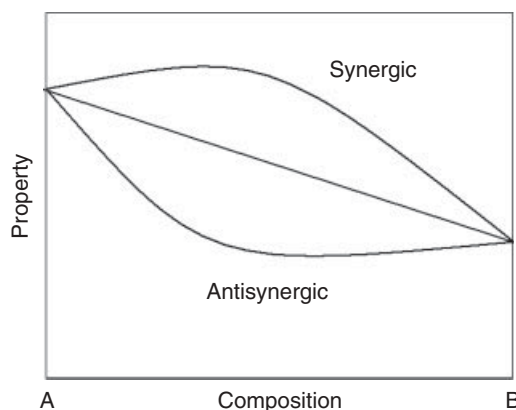


Figure 27.8 Schematic representation of blend property as a function of blend composition.

matrix of the other. On a macroscopic scale, the blend may appear heterogeneous and in the extreme case delaminated. When two immiscible polymers are blended with compatibilization, one may expect a synergistic combination of properties from each polymer [2, 14].

In most cases, melt mixing two polymers results in blends that are weak and brittle. The incorporation of a dispersed phase into a matrix mostly leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases.

The mechanical properties and end-use performance of a blend have been improved by compatibilization. From a practical point of view, a blend is often considered to be compatible if a certain set of mechanical properties is achieved.

The well-known examples of blends are impact modified, toughened polymers, where polymers with different glass transition temperatures are blended, such as a rubber with a thermoplastic. Many other blends are known, such as barrier polymers for packaging, where specific polar or non-polar polymers improve the properties of polymer blends, combined to increase the resistance against transport of water and a certain gas (oxygen, carbon dioxide, etc.), such as PA (barrier to oxygen) with a polyolefin (barrier to water vapor).

The incorporation of rubber particles within the matrix of brittle plastics may enormously improve their impact resistance. When a force is applied to a blend, several deformation mechanisms of the major phase and of cracks that are formed in the blend are important. Their relative importance may depend on the polymer and on the nature of the loading. The best-known effect from compatibilization is the reduction of the interfacial tension in the melt. This causes an emulsifying effect and leads to an extremely fine dispersion of one phase into the other. A second effect is the increase of the adhesion at phase boundaries giving

improved stress transfer. For this effect, the interaction between the compatibilizing copolymer chain and the polymer chains of the dispersed phase and the matrix phase will be important. The third effect is the inhibition of coalescence of the dispersed phase by modifying the phase boundary interface.

The change induced in the stress–strain behavior by incorporation of elastomeric particles into a PS matrix has been reported [15]. On toughening, PS brittle behavior changes into ductile with flow. The rubber-modified polymer absorbs considerably more energy; thus, higher elongation to break can be achieved. By contrast, an addition of rigid resin to a ductile polymer enhances the modulus and the heat deflection temperature.

In general, two mechanisms are responsible for plastic deformation in rigid polymers: crazing and shear yielding. Crazing is an important source of toughness in rubber-modified thermoplastics. A craze can be described as a layer of polymer, a nanometer to few micrometers thick, which has undergone plastic deformation approximately in the direction normal to the craze plane as a response to tension applied in this direction. Shear yielding is a mechanism in which a thin layer of polymer deforms in shear at constant volume. It is characterized by regions of sheared polymer oriented to the tensile or compression stress. Unlike crazing, shear flow is essentially a process continuous in space. Shear yielding is much less sensitive to environmental effects. Both crazing and shear yielding involve the absorption of energy, and most methods of toughening polymers involve modifying the polymer such that more crazing and shear yielding take place. The rubber-modified polymer absorbs considerably more energy in a tensile test because of its higher elongation to break, which can be achieved only as a result of yielding in the matrix. The rubber particles accelerate yielding by acting as stress concentrators initiating deformation in the matrix; secondly, they respond to the hydrostatic component of the stress by cavitating and increasing in volume, thus allowing the strain in the matrix to increase; and thirdly, in their cavitated and extended state, they stabilize the yielded polymer by carrying a share of the applied stress. Various types of response of the rubber particles have been observed experimentally as the polymer yields, which includes debonding between rubber and matrix, cavitation within the particle, crazelike fibrillation of the rubber phase, and crazing within subinclusions.

The mechanisms of deformation under tension of polymer blends are strongly related to the behavior of the microdomains and their adhesion to the matrix. It has been demonstrated that the formation of microcavities under tension tests is responsible for the propagation of fractures. Most homopolymers have a limited range of stable fatigue-crack growth. However, the range of stable fatigue-crack growth can be increased by blending

rubber particles or some organic filler into the polymer matrix. Rubber particles provide a crack-tip mechanism that involves rubber-particle cavitations and matrix plasticity. The crack growth rate may be affected by several external parameters such as a change in mean stress, variation in stress amplitude, and the presence of a notch in the sample.

Theoretical understanding regarding toughening mechanisms has been advanced for both rubber and thermoplastic toughened blends. Some theories based on the early toughening mechanisms of toughened thermoplastics suggested that the energy absorbed in a fracture is the sum of the energy required to fracture the matrix and to break the rubber particles. Microcracks due to rubber particles cause tensile yielding and, thus, a large tensile deformation. Voids result when the microcracks open, and these voids permit large strains. Debonding or microcracking effectively lowers the modulus in the frontal process zone around the crack tip and, thus, effectively reduces the stress intensity there. This theory [16] cannot explain many phenomena, such as stress-whitening, the large amount of plastic deformations, higher fracture toughness at a higher temperature, and the fact that nonreactive rigid thermoplastic particles may also toughen some systems. Another theory [17] proposes a mechanism that involves dilatational deformation of the matrix and cavitation of the rubber particles in response to the triaxial stresses near the crack tip, combined with shear yielding between the holes formed by the cavitated rubber particles. The stress-whitening was attributed to light scattering by these holes, and the major energy absorption mechanism was suggested to be the plastic deformation of the matrix. Plastic deformation blunts the crack tip, which reduces the local stress concentration and allows the material to support higher loads before failure occurs. Other authors have proposed that additional crack-tip shielding in rubber-modified resins occurs due to the reduction in yield stress by the stress concentration of the compliant rubber particles that facilitate shear yielding. Even though there are various toughening mechanisms proposed by different researchers, it seems that a single theory cannot explain every experimental result and phenomenon of toughening. Figure 27.9 shows a scheme that describes the several toughening mechanisms involved in the fracture of rubber-toughened polymer blends.

27.7.2 Rheological Properties

The rheology of polymer blends has received a lot of attention because of its technological importance in polymer processing. Rheology studies can be classified into three groups: studies dealing with the rheology of polymer mixtures in, respectively, homogeneous, phase-separated, and transition regimes. Research on homogeneous blends is focused mainly on the concentration dependence of viscosity and linear dynamic properties [6, 18–20]. Rheological

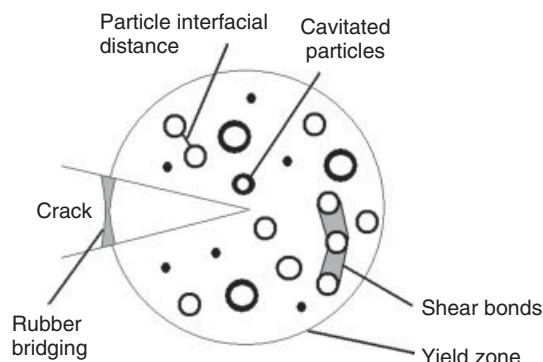


Figure 27.9 Scheme of the different mechanisms involved in the fracture of rubber-toughened polymer blends.

properties can be studied by taking into account the differences in molecular shape of the components. It is important to note that the TTS is applicable when polymer blends are in the homogeneous state far from the transition temperature and there is no obvious dynamic asymmetry of the components. In phase-separated polymer blends, the polymer blends show pronounced elastic properties, very long relaxation times, and a failure of the TTS. Complex changes in the linear viscoelastic properties were observed when polymer blends of a given composition were heated (for LCST systems) or cooled (for UCST systems) from the homogeneous regime to the phase separation regime.

When the size of dispersed particles is in the submicron range, fluid particles will remain spherical mainly because of the influence of interfacial tension. This system will have many common characteristics with dispersions of rigid particles.

When both phases are fluid, such as melt polymer blends, no general predictions of macrorheological behavior can be established. Generally, two distinct morphologies are observed, with the dispersed phase distributed either as ribbons or droplets. Droplets appear to be less deformable than an equivalent viscous Newtonian droplet. The resistance to breakdown in shear often makes most intensive shear mixers ineffective and leads to the need of employing other flow fields different from shear to achieve a good dispersion.

Morphology of a blend will depend on the detailed processing history. Morphologies such as ribbon type are stable in flow only if preserved by crystallization or quenching, and this type of morphology will break up rapidly when the flow ceases. This may affect the final properties of the final sample depending on if it was prepared by extrusion or injection molding. The great variety of morphologies observed in polymer blends has been attributed to the viscoelasticity of each polymer component.

Some authors report the next guide principles that may be applied for blend morphology after processing. (i) Drops with viscosity ratios higher than 3.5 cannot be dispersed in shear but can be in extension flow instead. (ii) The larger the interfacial tension coefficient, the less the droplets will deform. (iii) The time necessary to break up a droplet (T_b) and the critical capillary number (Ca_c) are two important parameters describing the breakup process. (iv) The effect of coalescence must be considered even for relatively low concentrations of the dispersed phase.

The addition of compatibilizers to polymer blends extensively affects their flow behavior. Chemical reactions occurring between the components of the blend upon compatibilization generally increase the viscosity of the system. Normally, the melt viscosity of polymer blends shows three types of behavior: (i) positive deviation behavior, where the blend viscosities show a synergist behavior, that is, blend viscosity is higher than the log additivity value; (ii) negative deviation behavior, where the blend viscosity shows a negative deviation from log additivity values; and (iii) a positive–negative deviation behavior. In the last case, the same blend exhibits both positive and negative deviation behavior depending on the composition, morphology, and processing conditions.

27.7.3 Optical Properties

Optical properties of blends have been studied to determine the factors leading to turbidity and hence to the design of blends with superior appearance. The analysis of the scattering of light and X-ray provides information about the morphology of the blends, allowing to measure the size and shape of the domain, as well as the differences in refractive index or electron density between components.

27.7.4 Barrier Properties

Polymer blending has been established as an effective means for building up new properties gradually altering transport properties of polymeric materials. Examples include blends of nylon and polyethylene that exhibit combined permeability to water vapor and oxygen, which in some cases is lower than the permeability to either component.

As the molecular size of most gases is much smaller than any scale of structure expected in polymer blend morphology, diffusion and permeability of gases can be employed to determine the phase behavior of a polymer blend. Therefore, the study of transport phenomena in blends would be motivated not only by the requirements of producing improved barrier materials but also by the continuous interest in the nature and characterization of polymer blend morphology.

27.8 APPLICATIONS OF POLYMER BLENDS

The worldwide commercialization of polymer blends has been directed at the replacement of traditional materials, such as metals and ceramics. Even though plastics can be more costly than other types of materials on a weight basis, they are often more economical in terms of production and manufacturing cost, mainly attributed to the less complex assembly of plastic parts that can be easily formed in complex-finished shapes [1, 21–26]. Blending is a convenient route to the time-efficient and cost-effective upgrading of commodity resins and to the tailoring of these resins to specific performance profiles for the desired application. The most common polymer blends and their applications are described below.

PPE/HIPS (Polyphenyl–Ether/High Impact Polystyrene). This type of blend features good dimensional stability, impact resistance, high resistance to moisture, low temperature impact strength, low creep, and improved processing. Applications include automotive instrument panels, interior trim, business equipment chassis, appliances, and electrical applications, including those requiring flame retardancy, building and construction, and medical applications.

PPE/PA. It features good chemical resistance, high continuous use temperature, high deflection temperature under load (DTUL), ease of processing, high modulus, and high impact. Applications include injection-molded automotive body panels, thermoformed truck body panels, trim components, mirror housings, wheel covers, under-the-hood electrical connectors, conductive grades for electrostatic painting, and fluid handling.

PET/PBT (Polyethylene Terephthalate/Polybutylene Terephthalate). Good colorability, excellent surface aesthetics, chemical resistance, gloss, good impact, and electrical properties. Applications include appliances, electrical applications, building, and construction.

PBT/Elastomers. It features chemical resistance, high notch Izod impact strength, and heat resistance.

PET/Elastomers. This blend features good stiffness, impact strength, and processability. Applications are in the automotive sector, such as in body parts, steering wheels, and under-the-hood components.

PET/PSF (Polyethylene Terephthalate/Polysulfone). It features warp resistance, stiffness, dimensional stability, high temperature performance, and chemical resistance. Applications include industrial process equipment, electrical connectors, and food-processing equipment.

PC/ABS (Polycarbonate/Acrylonitrile–Butadiene–Styrene). It has good heat resistance, toughness, tensile strength, creep resistance, color stability, flame resistance, moldability, and surface appearance. It is used in business

machine housings, exterior automotive trim, wheel covers, IPs, and interior parts. This blend replaces over-engineered straight PC in applications where a higher heat or impact resistance than straight ABS is required. Eliminating painting with a low gloss provides cost reduction, elimination of volatile organics, and better recyclability.

PC/PBT. It has low temperature impact, dimensional stability, and chemical resistance. It is applied in automotive bumpers.

PC/PET. This blend is transparent; it shows low temperature performance, chemical resistance, abrasion resistance, and impact resistance. Applications are in automotive parts, such as bumpers and exterior trim, in furniture, such as chair arm rests, support members, in appliances (housings), hand tools (housings), lawn and garden, such as motor housings, guards for electric hedge trimmers, and protective housings. Industrial applications include fluid handling equipment such as pump housings, valve bodies, and handles, as well as in electricals/electronics such as coil bobbins and connectors.

PC/TPU (Thermoplastic Polyurethane Elastomer). It is used in exterior motor vehicle for chemical resistance and strength.

PA/ABS. It has high temperature warp resistance, chemical resistance, good processability, and superior appearance. It can be applied in automotive parts such as body panels, under-the-hood connectors and components, fuel tanks, bearings, bushings, and cams.

PA/PE. It exhibits chemical resistance to gasoline and is used in fuel tanks.

PA/PTFE (Polyamide/Polytetrafluoroethylene). It shows low coefficient of friction and high temperature resistance. It is used in mechanical parts such as bearings, bushings, thrust washers, and construction hardware such as door latches.

TPU/ABS. It has low temperature toughness, chemical resistance, abrasion resistance, and superior toughness.

POM/Elastomer (Polyacetal or Polyoxymethylene). It has toughness, good notched Izod resistance, and chemical resistance. It is used in interior automotive, gears, cams, etc.

PPS/PTFE (Polyphenylene Sulfide/Polytetrafluoroethylene). It has high durability and wear resistance, tensile strength, hydraulic stability, and heat resistance. Applications include seals, valves, and bushings.

PE/PIB (Polyethylene/Polyisobutylene). It is used in sheet and film for barrier properties.

PE/Ionomer. It has impact resistance, stiffness, and heat resistance, and it is easy to process.

PP/EPDM, PE/EPDM (Polypropylene/Ethylene–Propylene–Diene–Monomer). It shows low temperature performance and toughness; rubberlike; used in wire and

cable insulation, hose and tubing, interior automotive trim, and mechanical components.

PVC/CPE or PVC/EVA (Poly(vinyl Chloride)/Chlorinated-Polyethylene) or (Poly(vinyl Chloride)/Ethylene-Vinyl Acetate Copolymer). They have impact resistance and UV stability and are used in the construction industry as siding, pipes, conduit, foamed material, and rigid sheets.

PVC/NBR (Nitrile Rubber). It exhibits oil and other organic fluid resistance and is used in hoses, belts, wire and cable insulation, and appliance parts.

PVC/TPU. It shows thermal stability, chemical resistance, and low temperature flexibility for footwear.

PVC/PMMA (Poly(Methyl Methacrylate)). This blend sometimes includes a small amount of MMA copolymer to improve the melt strength and as a processing aid. It is used in business machine housings, furniture, mass transit seating, and food service trays. MBS or MABS (methacrylate acrylonitrile butadiene styrene) can be added to improve low temperature toughness. Improved grades are used in siding, pipe, and fittings.

SAN/EPDM (Styrene acrylonitrile). It has good weatherability, impact strength, chemical resistance, and good processing. It is used in construction products and sporting goods.

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