CHAPTER II

THEORY

2.1 Polymer Blends

The term polymer blend refers to a mixture of at least two polymers or copolymers. The polymer blends may be homogeneous or heterogeneous on a microscopic scale, but it should not exhibit any obvious inhomogeneity on a macroscopic scale.

The compatibility of a polymer-polymer system determines a polymer system property. Compatibility and incompatibility refer to the degree of intimacy of the polymers in the blend, which depends on the method of measurement employed in the examination. In practice, compatible polymer blend is a homogeneous polymer mixture to the eye with physical properties frequently enhanced over the constituent polymers. Polymer blends that are heterogeneous on a macroscopic level are called incompatible polymer blends.

Under microscopic level, a miscible polymer blend is a polymer mixture which is homogeneous down to the molecular level. Thermodynamically, this is associated with the negative value of the free energy of mixing, i.e. $\Delta G_m \cong \Delta H_m \leq 0$; where ΔG_m is the Gibbs' free energy of mixing and ΔH_m is the enthalpy of mixing. Miscible polymer blend has a single phase, as shown in Figure 2.1(a). In order to be miscible, some attraction between the two polymers must be present to overcome partially the intramolecular cohesive forces of the individual polymer. Interpolymer attractions result from specific interaction between functional groups on polymer-A with different functional groups on polymer-B. This condition, however, rarely occurs, and only few polymer blends are totally miscible.

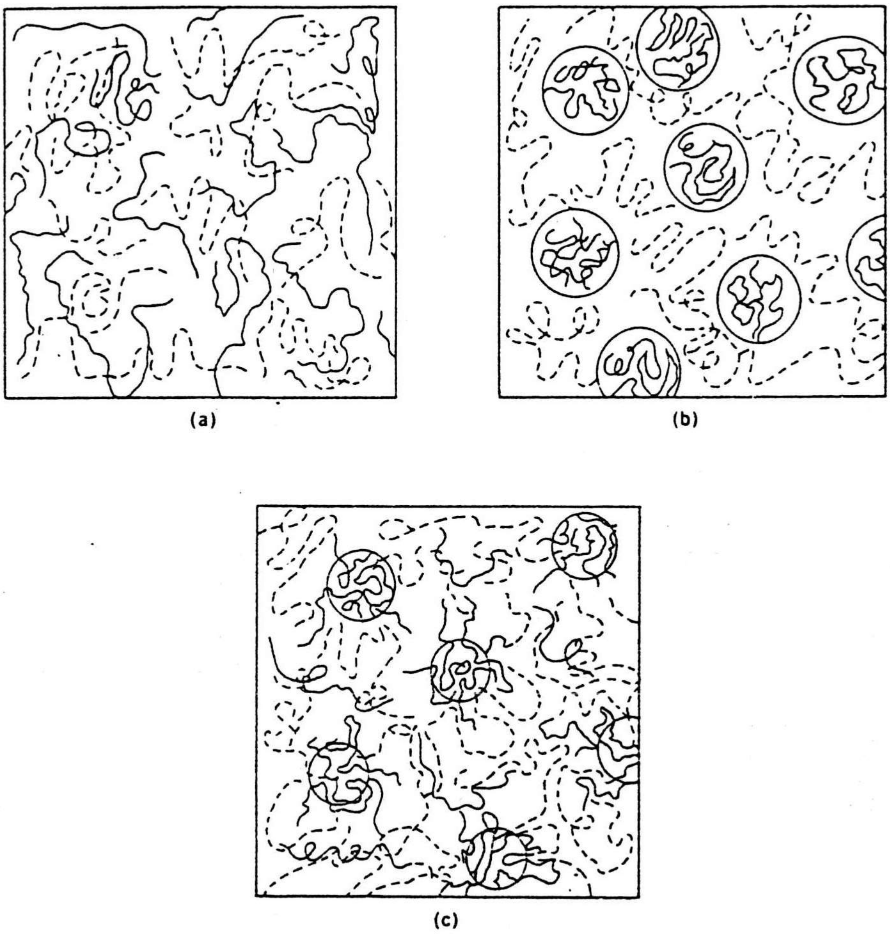


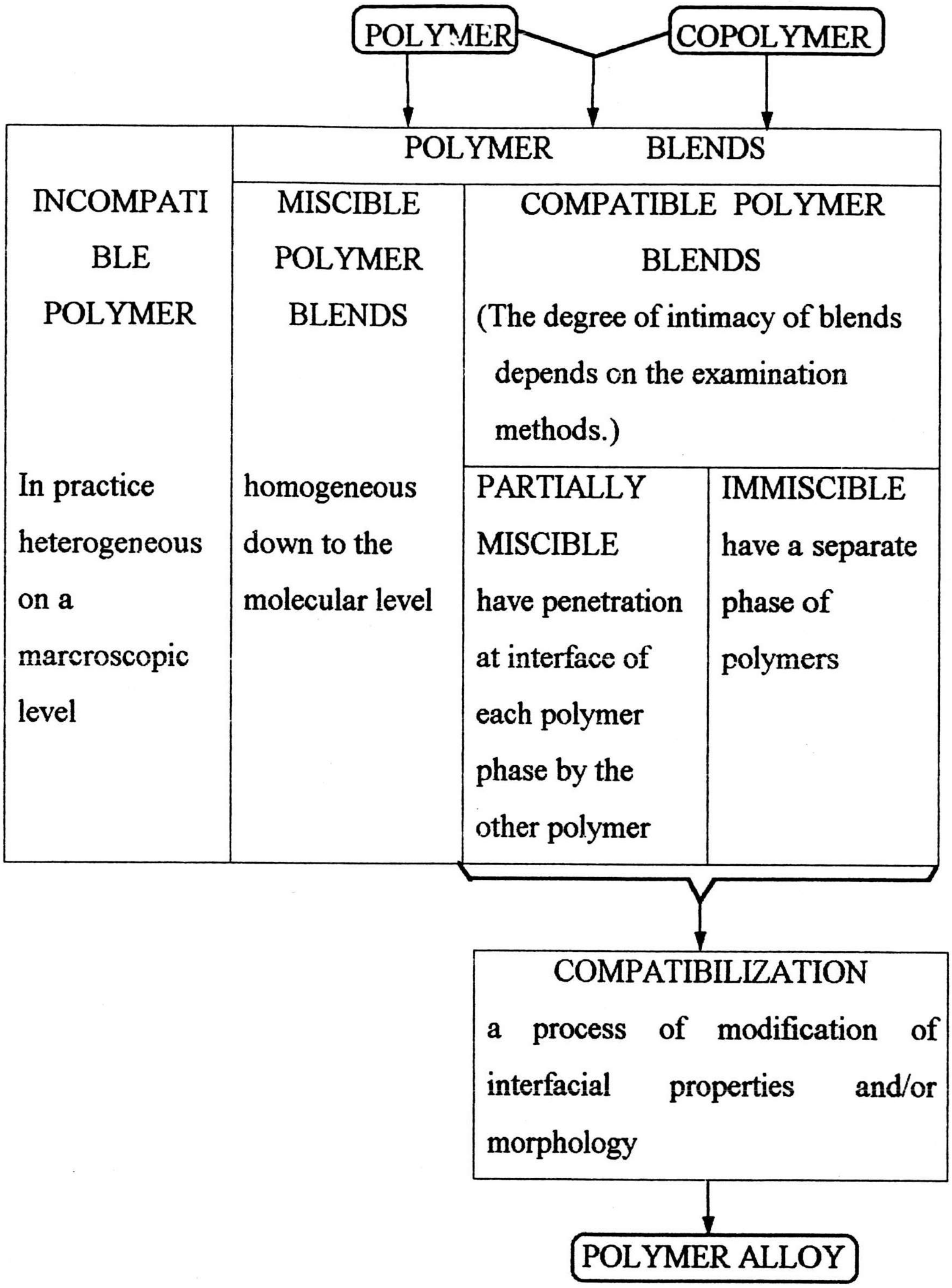
Figure 2.1: Morphologies of a blend of polymer-A (solid lines) and polymer-B (dashed lines); (a) miscible; (b) immiscible and (c), partially miscible.

An immiscible polymer blend is a polymer mixture in which polymer-A forms a separate phase from polymer-B. Thermodynamically, this is associated with the positive value of the Gibb's free energy of mixing, i.e. $\Delta G_m \cong \Delta H_m \geq 0$. Its morphology is shown in Figure 2.1(b). The polymer present in the lower concentration usually forms a discontinuous or discrete phase, whereas the polymer present in the higher concentration forms a continuous phase.

Frequently, a blend of two polymers is neither totally miscible nor totally immiscible, but it falls somewhere in between. A polymer blend of this type is partially miscible. Partially miscible polymer blends may form completely miscible polymer blends when either polymer is present in small amounts. At compositions where a partially miscible polymer blends are in two phases, the phases may not have a well-defined boundary since polymer-A molecules can significantly penetrate into the polymer-B phase and vice versa, as depicted in Figure 2.1(c).

The term compatibilization refers to a process of modification of the interfacial properties of an immiscible or a partially miscible polymer blend and leading to the creation of a polymer alloy. On the other hand, polymer alloy is an immiscible polymer blend having a modified interface and/or morphology.

The polymer blend nomenclature may be concluded in the form of a diagram as illustrated in Figure 2.2. In general, however, the terms polymer blends and polymer alloys are now used interchangeably.



(The degree of intimacy of blends depends on the examination methods.)

In practice heterogeneous on a marcroscopic level

homogeneous down to the molecular level

have penetration at interface of each polymer phase by the other polymer

have a separate phase of polymers

a process of modification of interfacial properties and/or morphology

Figure 2.2: Interrelations in polymer blend nomenclature.

A polymer alloy can be subdivided in two categories: (i) those in which the compatibilization leads to very fine (usually sub-micron) dispersion so the molded part will show neither streaking nor excessive weld-line weakening and (ii) those where some compatibilizer is added in order to facilitate the formation of the desired morphology in a subsequent processing step.

2.2 Determination of polymer/polymer miscibility

There are numerous techniques that can be used to determine compatibility of polymer blends. Each technique has a limit of useful ranges. Some techniques can determine whether the polymer blends are miscible, immiscible or partially miscible. Some techniques may determine only whether the polymer blend is a miscible blend or not. Approximate limits of useful ranges of the techniques to study the blend morphology are shown in Figure 2.3 [2].

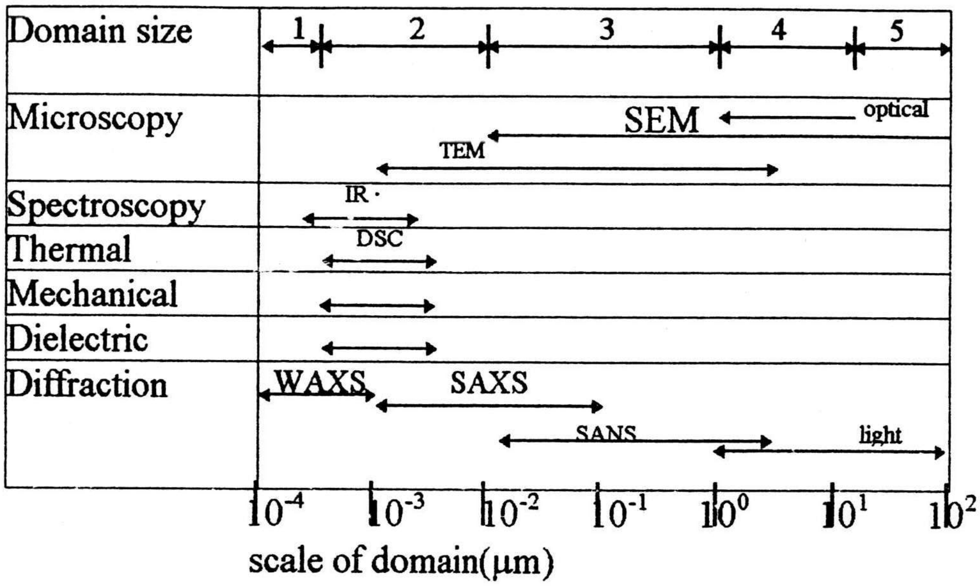
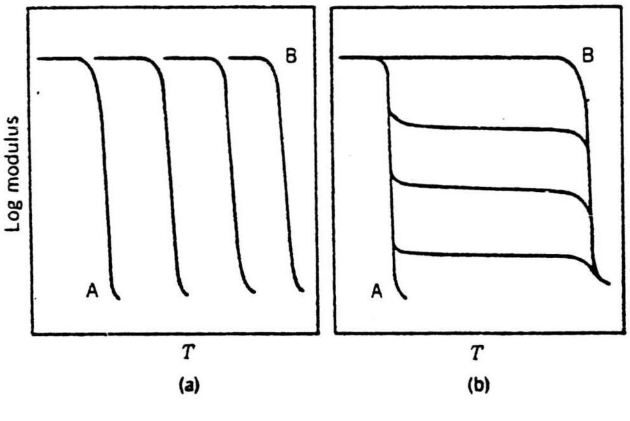


Figure 2.3: Approximate ranges of experimental techniques to study blend morphology of: (1) interatomic; (2) molecular, spherulites; (3) filler aggregates, compatibilized blends; (4) reinforcements, noncompatible blends and (5) voids.

A variety of experimental techniques have been used to determine the compatibility of polymer blends. Some techniques, such as caloriemetry, thermomechanical, dynamic mechanical procedures, are based on the determination of the number and the location of the glass-transition temperature; T_g. Other techniques are based on scattering or microscopy techniques.

2.2.1 Glass-transition Temperature

The glass-transition behavior is a simple and usually reliable method for determining whether a blend system is miscible. It is examined by thermal, mechanical, dielectric or similar techniques. The glass-transition temperature (T_g) of a polymer is the temperature at which the molecular chains have sufficient thermal energy to overcome attractive forces and move vibrationally and translationally. The number and the locations of the T_g's provide much insight into the nature of the polymer blend. For example, a miscible one-phase blend should have only one T_g which is composition dependent and reflects the mixed environment of the blend. A two-phase blend should have two glass transitions, one for each phase. Figure 2.4 illustrates this by showing how the modulus varies with temperature for miscible and immiscible blends of varying proportions of two completely amorphous polymer-A and -B.



(a) (b)

Figure 2.4: Effects of composition on the temperature dependence of the modulus or the stiffness of (**a**) miscible and (**b**) immiscible blends of polymers -A and -B, both of which are amorphous.

The method of detecting the miscibility or the immiscibility of a polymer blend system by the glass transition temperature has a limited usefulness when the glass transition of the two polymers are very close and cannot be adequately resolved. Similarly, crystallization of one of the polymers during the T_g measurement may interfere with the analysis. A blend of two polymers often appear to have a single T_g by thermal analysis, but microscopic inspection reveals two phases. Although two distinct T_g's occur, they are superimposed and make this T_g hard to detect. It is common to find the glass transition of blends to be broader than that of the pure components owing to composition fluctuations in the mixture.

The T_g is usually determined by a differential scanning calorimetry (DSC). This thermal-analysis technique yields a plot of the differential heat absorbed or dissipated by the sample compared with a reference; the temperature of both the sample and the reference is raised at a constant rate. An inflection is observed at the T_g because an increase in the specific heat of the polymer is accompanied by the increased molecular motion. With miscible one-phase blend, only one T_g is observed at a temperature which lies between those of the constituent pure polymers, as shown in Figure 2.5.

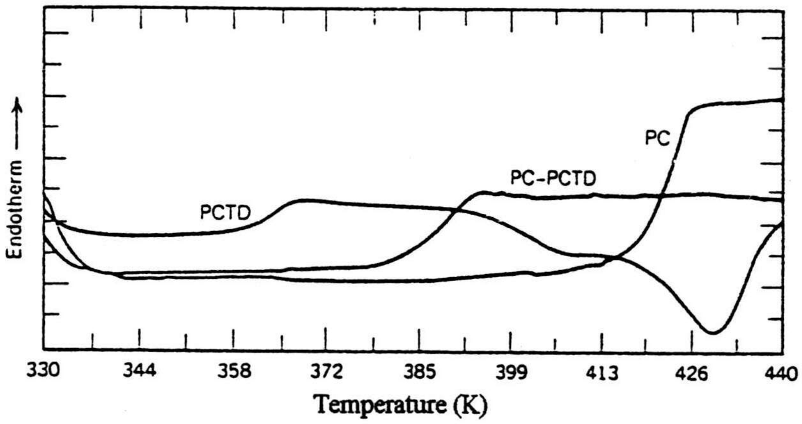


Figure 2.5: DSC thermogram of a miscible one-phase 50:50 blend of polycarbonate (PC) and poly(cyclohexane-1,4-dimethanol-*co*-terephthalate-*co*-isophthalate) (PCTD).

For immiscible two-phase systems, two T_g's that closely approximate those of the individual polymers are expected. This is shown in Figure 2.6.

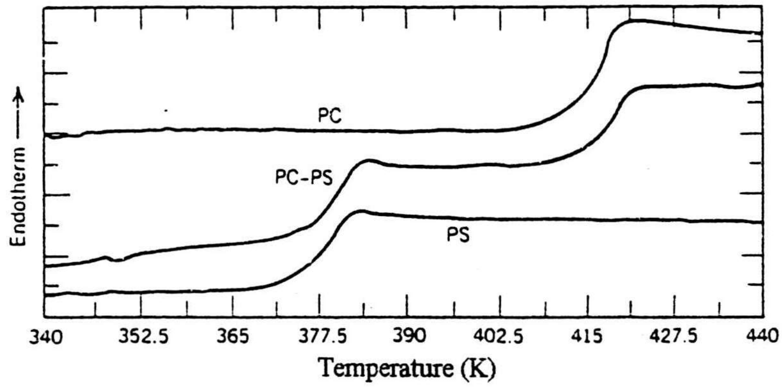


Figure 2.6: DSC thermogram of an immiscible one-phase 50:50 blend of polycarbonate (PC) and polystyrene (PS).

The third kind of blend system is a two-phase partially miscible blend. This blend, like the two-phase completely immiscible blend, also shows two T_g's. However; the different is that the T_g's of this system fall between those of the individual polymers. The T_g of the higher T_g component is lowered whereas that of the lower T_g component is raised because some molecular miscibility has taken place.

2.2.2 Scattering

A quick but not totally reliable method to determine that a polymer blend forms a single phase or multiphase is by its transparency. Discontinuous domains in the polymer blends are often large enough to refract light, forming a translucent or an opaque blend when two transparent polymers are mixed. In a miscible one-phase blend of two amorphous polymers (transparent polymers), no domains are present to refract light and hence the blend may be transparent. A plot of the transparency against the amount of PC in miscible PC-PCTD blend and immiscible PC-PETG blend is shown in Figure 2.7.

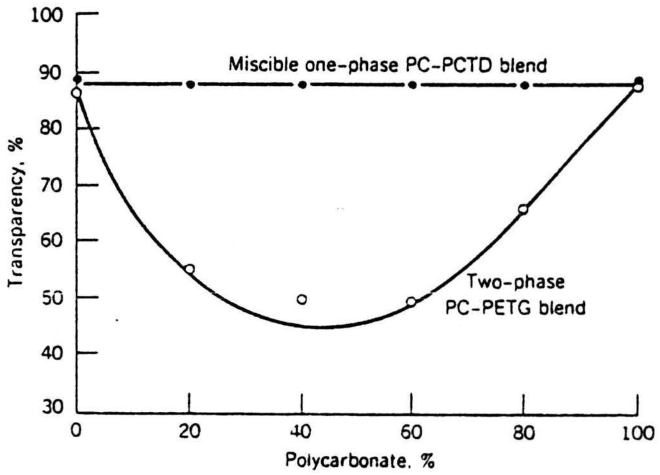


Figure 2.7: Transparency plotted against the composition for blends of PC with PCTD and PC with PETG or poly(ethylene glycol-co-cyclohexane-1,4-dimethanal terephthalate).

By the scattering method, one may reach erroneous conclusions if

a) the refractive indexes of polymer A and polymer B are similar.

b) the domains are smaller than that of the wavelength of light, the light is not scatted, and a two phase blend can be transparent.

c) either component of an initially transparent miscible blend later crystallizes, the blend may become opaque.

To improve this technique, the use of an x-ray and a neutron scattering provide much insight into the blend morphology. Furthermore small-angle neutron scattering has emerged as a powerful tool for investigating many aspects of polymer blends. It can be used to obtain the thermodynamic interaction energies for miscible blends. However, one of its most unusual aspects is the ability to determine conformational information on the components.

2.2.3 Microscopy

Microscopy is a useful tool to determine whether a blend is single phase or multiphase. It is best applied to systems where the phases can be differentiated from one another by chemical or physical treatment such as staining or solvent swelling.

2.3 Methods of Blending

Preparation of polymers blends can be accomplished by three main methods.

2.3.1 Melt mixing

2.3.1.1 Mechanical mixing

The polymer mixture is melted and blended on an open roll, in an extruder or any other suitable intensive mixer.

2.3.1.2 Mechano-chemical mixing (Reactive mixing):

This is similar to the mechanical mixing but there is a reaction involved during mixing. Mechano-chemical mixing may lead to a true chemical graft or block copolymer of the parent polymer.

Several equipments can be applied for polymer blending. The advantages and the disadvantage of the various blending or alloying equipments are listed in Table 2.1.

Table 2.1: Advantages and disadvantages of various blending or alloying equipments.

Machines	Advantages	Disadvantages
Twin-screw extruder	Uniform high shear stress flow, short residence time, self-cleaning, flexibility and ease of change	Capital cost
Single-screw extruder	Cost, availability, flexibility for modification of screws and add-ons	Poor control, low rate of shearing, long residence time, dead-spaces
Internal mixer	Uniformity of stress history control	Capital and operational cost, batch to batch variation
Multi-stage system	Flexibility, control, uniformity	Capital cost (for large diameter machine, the uniformity of temperature can be poor)

2.3.2 In situ polymerization

In situ polymerization involves polymerization of a monomer which acts as a solvent in a solution of another polymer in that polymer solution. The resulting blend forms an interpenetrating polymer networks (IPN's). The product of this method is called a chemical polymer blend.

2.3.3 Solution blending

Solution blending is performed by dissolving polymers as a polymer mixture in a co-solvent (common solvent) then film casting, freeze drying or co-precipitation the polymer mixture. In this case, the polymer blends are made by mixing and coagulating two different kinds of polymer latexes, the resulting product is called latex polymer blend.

Based on the corresponding method of preparation, polymer blends can be classified as shown in Figure 2.8. Table 2.2 compares the advantages and the disadvantages of the aforementioned blending methods.

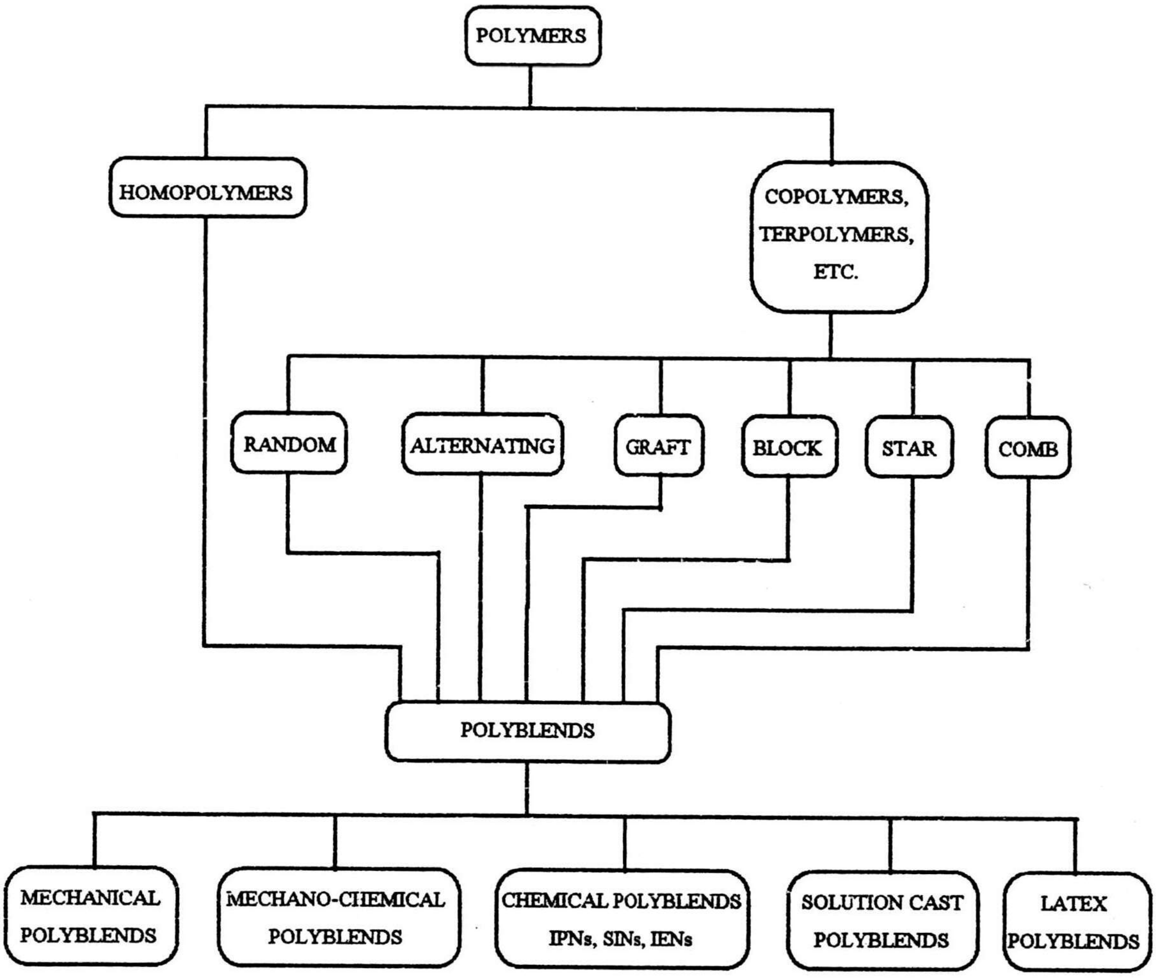


Figure 2.8: The polymer mixtures are classified in terms of their method of preparation.

Table 2.2: The advantages and the disadvantages of each blending method.

Method	Advantage	Disadvantage
Melt mixing	-close to condition used in processing -interchange reaction may occur during melt mixing, giving a copolymer which improves compatibility	-high melt viscosity -freedom of molecular motion is low -efficiency of molecular mixing is low -approach to equilibrium molecular mixing is slow and difficult
Solution blending	-high freedom of molecular motion -high efficiency of molecular mixing -approach to equilibrium molecular mixing is fast and relatively easy -for polymer not amenable to melt processing	-offer other opportunities for misleading results -must consider the effect of common solvent , e.g. shape of polymer molecule in solution which depend on polymer-solvent interaction.
In situ polymerization	-graft copolymer that form in situ polymerization may act as a "compatibilizer".	-it takes long time to polymerize because of the increasing viscosity of mixture

(a) a blend of two miscible polymers may form a two-phase mixture when cast from certain solvent because of different in solvency power for the two polymer.
(b) two immiscible polymers form a single-phase solution when diluted enough by solvent, and extremely rapid solvent removal, as in freeze-drying, can trap the polymers in a non-equilibrium homogeneous state.

2.4 Properties of polymer blends

In the simplest case, the properties of the polymer blends reflect a composition-weighted average of the properties possessed by the components. However, the property dependence on composition varies in a complex way with the particular property, the nature of the components (glassy, rubbery, or semicrystalline), the thermodynamic state of the polymer blends (miscible or immiscible), and its mechanical state (whether its molecules and phases are oriented by the shaping of the material for testing).

2.4.1 Miscible blends

2.4.1.1 Thermal properties

Miscible binary blends of amorphous polymers have only one phase and their properties are easily related to those of the blends components. On the property-composition diagram illustrated in Figure 1.9, the glass transition temperature, (T_g), usually falls below the tie-line connecting the T_g's of the pure components in accordance with Fox equation as shown in Equation (2.1) [3], which was originally written to describe the composition dependence of the T_g for the copolymer.

$$\frac{1}{T_g} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}} \qquad (2.1)$$

where T_g = glass transition temperature of the mixture
W_i = weight fraction of the *i*th component
$T_{g,i}$ = glass transition temperature of the *i*th component

Values above the tie-line have been reported in some noncommercial systems involving very strong intercomponent hydrogen bonds. The fact that the glass-transition temperature depends on the composition in their subclass has a considerable commercial significance because it largely determines the heat-distortion temperature (HDT) or the maximum-use temperature of the blends.

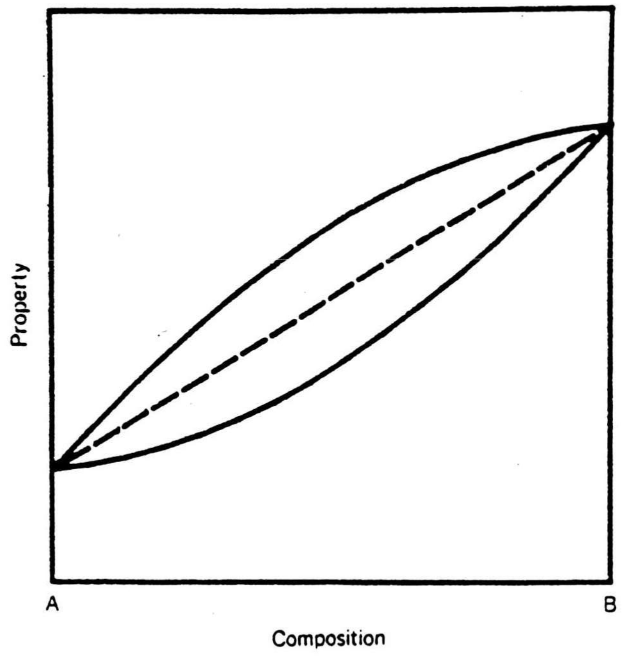


Figure 2.9: Typical property of a polymer blend is plotted against the composition for miscible blends of polymers-A and -B.

For miscible blends of crystallizable polymer, the melting point, T_m, shifts lower as predicted by Nishi-Wang Equation [4], as shown in Equation (2.2).

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \frac{-RV2}{\Delta H_2 V_1}\left[\frac{\ln \phi_2}{\gamma_2} + \left[\frac{1}{\gamma_2} - \frac{1}{\gamma_1}\right](1-\phi_2) + \chi_{12}(1-\phi_2)^2\right] \qquad (2.2)$$

where

T_m = Equilibrium melting temperature

T_m^o = Equilibrium temperature of Pure Component

V_1, V_2 = Molar Volume of amorphous and Crystalline components

ΔH_2 = Heat of fusion of 100% Crystalline part

γ_1, γ_2 = Degree of Polymerization

ϕ_2 = Volume Fraction of Crystalline Part

χ_{12} = Interaction Parameter of the blends

2.4.1.2 Mechanical properties

The mechanical properties of miscible polymer blends usually depend on particular properties of each component, the compositions of the blends, the morphology of the blends and the intermolecular force in the system.

The mechanical properties of an amorphous miscible system such as polyphenylene oxide (PPO)-polystyrene (PS) deviates from the tie-line behavior which are thought to arise from the suppression of the glassy-state relaxation resulting from the negative volumes and heats of mixing observed. Suppression of the glassy-state relaxation leads to strengths and elastic moduli above the tie-line when test at room temperature and to ultimate elongation and impact strength which lie below the tie-line. It was postulated that the intermolecular forces that create miscibility reduce the low temperature relaxation responsible for ductility and toughness.

The mechanical properties of miscible blends that contain a crystallizable component also depend on the state of crystallization of this component and on the thermal history of the material. For example, poly (vinylidene fluoride) (PVF_2) forms miscible blends with polymethylmethacrylate (PMMA), from which it crystallizes, provided it is present in sufficient quantity and that the rate of cooling from the melt is sufficiently low. At low PVF_2 contents, the crystallization rate is suppressed during cooling because the difference between the melting temperature of the PVF_2 and miscible blends T_g is small. Consequently, the blend is completely amorphous, and since the T_g of PVF2 is much lower than that of PMMA, the PVF_2 reduces the miscible blends T_g and plasticized the PMMA component. This reduces the strength and the modulus but increases the elongation at break with initial increase in the PVF_2 content. Furthermore addition of PVF_2 continues their trend until the T_g of the blends is reduced sufficiently and the PVF_2 content is high enough, i.e. > 40%, to allow it to crystallize. Continued addition of PVF_2 beyond 60% causes strength to increase and the ductlity to decrease as the crystalline portion of PVF_2, becomes the principal component. These effects of plasticization and crystallization completely mask the more subtle effects caused by component interaction noted in the previous discussion of the properties of miscible amorphous glasses.

2.4.2 Immiscible Blends

The mechanical properties of immiscible polymer mixtures, where each component in the blend is present as a separate phase, is different from those of miscible systems which generally depend on the composition.

2.4.2.1 Thermal property

When two immiscible polymers are mixed, the individual phase domains retain the glass transitions of their respective parent homopolymers, as shown in Figure 2.4. The result is that the blends exhibit two principal glass transitions, like that of the blocks, grafts and IPN's. While simple homopolymers, random copolymers and miscible polymer blends usually exhibit one principal glass transition, on the other hand, the melting temperature; T_m, of immiscible blend systems which have semicrystalline component, does not change.

2.4.2.2 Mechanical properties

The presence of multiple amorphous phases results in a different property with respect to composition than those of the miscible systems. For example, in amorphous immiscible binary mixtures, the stiffness, the strength, and the HDT properties of the principal component largely determine the properties of the blends, as illustrated in Figure 2.10. This is in contrast with the nearly linear composition dependence shown for miscible amorphous binary systems. It also suggests some advantages in forming immiscible blends. This advantage is somewhat reduced when miscible and immiscible blends in which the main component is semicrystalline are compared because the HDT is determined, in both cases, by the melting temperature (T_m) of the semicrystalline component. The T_m is only slightly depressed by the interactions responsible for miscibility. The mechanical properties of the immiscible mixtures, particularly those related to ductility, are related to the separate phase, the degree of adhesion between the phases and the morphology of the separate phases.

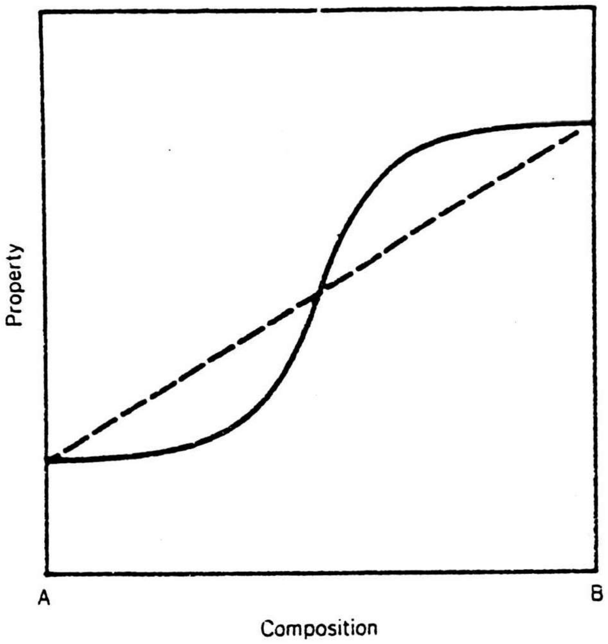


Figure 2.10: Property plotted against the composition profiles of immiscible (——) and miscible (-----) blends.

2.4.2.2.1 Interfacial adhesion

Poor elongation and low impact-strength properties are related to poor stress transfer between the phases of the immiscible-blends. Low molecular attractive or adhesion force between the blend components are responsible for the immiscible phase behavior. It is believed that the poor interfacial adhesion causes premature failure under stress as a result of the crack-opening mechanism.

2.4.2.2.2 Morphology

Blends ductility can be improved by using the rheological forces associated with flow processing to change the morphology of the dispersed phase from spheres to lamellar or ribbonlike structures with high surface areas and aspect ratio that are oriented in the load-bearing direction. By analogy with fiber-reinforced composites, this phase organization permits better stress transfer to occur despite low interfacial adhesion and geometrically minimizes the mode of failure associated with crack opening by an applied tensile load. Such non-equilibrium structures are highly process-dependent and may be lost in subsequent processing steps. The properties at right angles to the oriented direction are often poor. The process has significant effects on the phase geometry and properties in immiscible blends. Blending techniques and methods have also been employed to prepare co-continuous networks of phases. Co-continuous network have improved ductility because the continuous nature of the phases permit load sharing by the blend components without the need for high stress transfer across the phase boundaries.

2.4.3 Partially miscible or Compatibilized blends

2.4.3.1 Thermal property

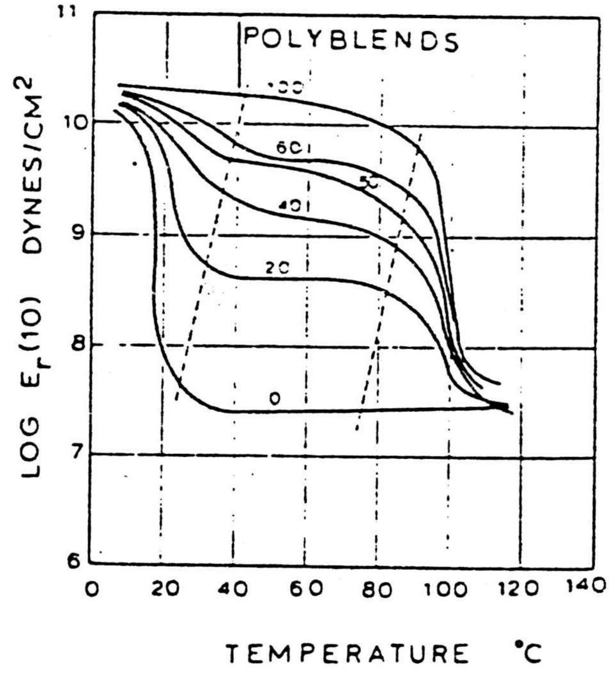


Figure 2.11: Modulus-temperature behavior of blends of polystyrene with a 30/70 butadiene/styrene copolymer. Dashed line delineates change in the T_g.

In partially miscible and compatibilized blends or alloy, significant molecular mixing occurs at the surface boundary while the immiscible blends have sharp boundary due to lack of molecular mixing at surface boundary. As a result, the glass transitions will be broadened and/or their temperatures will be closer together, as illustrated in Figure 2.11.

2.4.3.2 Mechanical properties

The mechanical properties of the immiscible blends must be evaluated in the light of the blend's morphology, interface adhesion and chemistry.

For compatible blends, the arrangement in space (structure) of the discrete regions (P) or domains in the continuous matrix (M) often has a major effect on the properties. In discussing the structure, as shown in Figure 2.12, it is convenient to distinguish between the dispersion [D] (fine to coarse) of the domains, which reflects primarily their size and number and their distribution [D'] [good to poor (agglomerates)] which in turn, reflects the uniformity throughout a sample. Furthermore, the blend morphology is stabilized by a compatibilizer.

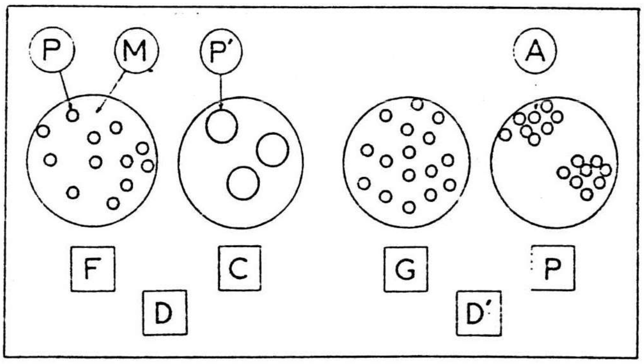


Figure 2.12: Phase dispersion and distribution of [D] Dispersion; [F] Fine Dispersion; [C] Coarse Dispersion; [D'] distribution; [G] Good distribution; [P] Poor distribution; (M) Matrix (first phase); (P) Small particles (second phase); (P') Large particles (second phase) and (A) Agglomerates.

In two-phase polymer systems such as a rubber toughened-plastic, the technical properties do not depend solely on the properties of the pure components. In a complex way, numerous parameters affect the technical properties of the final product as shown in Table 2.3.

MATRIX	FINISHED ARTICLE	SOFT COMPONENT
	STIFFNESS	TYPE OF RUBBER
	TOUGHNESS	
MOLECULAR WEIGHT	FLOWABILITY	PHASE VOLUME RATIO
	HEAT DISTORTION	PARTICLE SIZE
MOLECULAR WEIGHT DISTRIBUTION ⇨	STRESS CRACK RESISTANCE	⇦ PARTICLE SIZE DISTRIBUTION
ADDITIVE	GLOSS	PARTICLE STRUCTURE
	TRANSPARENCY	DEGREE OF GRAFTING
	WEATHERING RESISTANCE	CROSSLINKING DENSITY OF THE RUBBER PHASE

Table 2.3: Molecular and morphological parameters that influence technical properties.

2.4.3.2.1 Interfacial adhesion

Polymer-polymer adhesion plays a significant role in determining the ductility-related properties of two-phased polymer systems. Better adhesion between ductile and brittle components improves ductility. The extent of local or segmental diffusion across the thickness; *a*, as defined in Figure 2.13, can critically affect the mechanical strength of the adhesive bond.

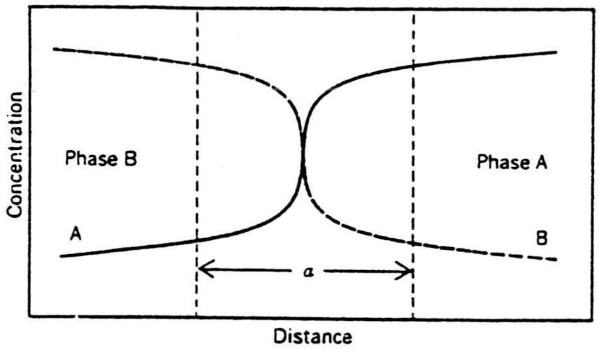


Figure 2.13: Composition profiles at a polymer-polymer interface and interface thickness; *a*.

Low segmental diffusion is the result of polymer-polymer immiscibility, or insolubility, and leads to sharp interface and poor bond strength. However, statistical thermodynamic theories predict that various degree of interdiffusion of polymer segments occur in the interfacial layer as required to minimize the interfacial energy. These theories predict that the characteristic interfacial thickness; *a*, is related to the Flory-Huggins interaction parameter; χ_{AB}, for a binary immiscible mixture by

$$a = c/(\chi_{AB})^{m} \qquad (2.3)$$

where c and m are slightly different constant, depending on the assumptions set in the derivation. Equation (2.3) clearly suggests that the interfacial thickness and the strength of the adhesive bond increases as the χ_{AB} value approach zero. For weakly interacting components, the χ_{AB} can be related to their solubility parameter as shown in Equation (2.4).

$$B_{12} \cong (\delta_1 - \delta_2) \quad (2.4)$$

$$\chi_{AB} = B/(RT) \quad (2.5)$$

where δ_1, $\delta 2$ solubility parameters of two homopolymers ; 1, 2.

B_{12} interaction energy density

Equation 2.5 implies that χ_{AB} approaches zero when the dispersive, polar and the hydrogen-bonding contributions to the component solubility parameters are nearly matched. The match between the component solubility parameters apparently needs to be close to achieve good adhesion. Polymer-polymer adhesion increases substantially and blends ductility properties improve when the polymer components are miscible or partially miscible, a circumstance corresponding to negative or small positive χ_{AB} values respectively.

2.4.3.2.2 Morphology

Besides the interfacial adhesion, the size of the domains and the degree of dispersion are also important for mechanical properties. In each type of matrix and domain, the optimum domain size range is different. The particle distribution should therefore be as homogeneous as possible.

The structure of morphology is determined partly by the nature of the component polymers and partly by the blending procedure and conditions as well as the final processing. The fine dispersion and good distribution of grains is achieved if a suitable compatibilizer and appropriate blending conditions are applied.

2.5 Phase inversion

The greatly different properties of polymer blends depend on which phase is the continuous phase. The most important factors determining the phase continuity include the melt viscosity (η) of each phase and its phase volume fraction (ϕ). Qualitatively, all other factors being equal, the phase with the larger volume fraction will be continuous. Similarly, the phase with the lower viscosity tends to be continuous, because it tends to flow around the higher viscosity phase. It is often observed that regions of phase inversion are bounded by an inverse relation between η_1/η_2 and ϕ_1/ϕ_2 .

Assuming symmetrical behavior of both the viscosity and the volume fraction, a semi-empirical rheological equation expressing the phase inversion region may be written for phases 1 and 2 as following:-

$$(\eta_1/\eta_2) * (\phi_1/\phi_2) \approx 1 \qquad (2.5)$$

If the quantity on the left is greater than unity, phase 2 is likely to be continuous. If the aforementioned quantity is less than unity, phase 1 is likely to be continuous.

This equation is designed for experiments in the limit of low shear rate. However, sufficient shear is implied to allow thermodynamically more stable morphology to occur. When the product $(\eta_1/\eta_2) * (\phi_1/\phi_2)$ is approximately unity, dual-phase continuity is encouraged.

The application of the relationship shown in Equation (2.5) is illustrated in Figure 2.14 for several series of mechanical blends. Three regions of space are developed: the filled point represents phase 1 continuous; the open point represents phase 2 continuous and the half filled point indicates dual phase continuity.

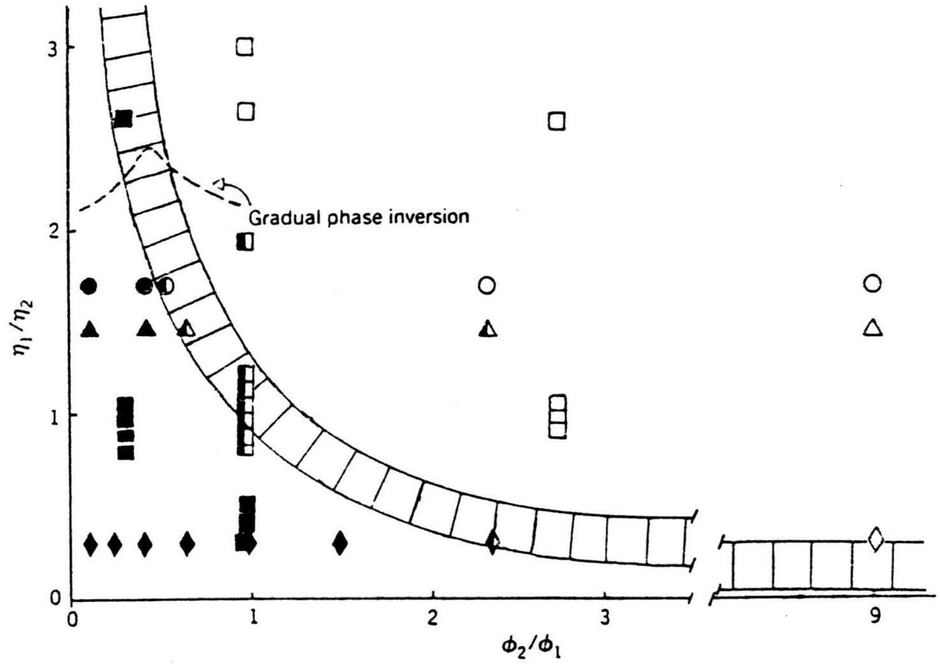


Figure 2.14: An idealized phase continuity diagram for mechanical blends.

○ PB(55%)/PS　　△ PB(35%)/PS

□ EPDM/PB　　◊ ABS/Polysulfone

Note: 35% and 55% refer to two viscosity grades of the polybutadiene. Filled points represent phase 1 continuous; open points represent phase 2 continuous and the half-filled points represent dual-phase continuity.

Important aspects of the phase inversion may be followed by changes in the modulus of a multicomponent polymer system, especially if the module of the two component polymers differ significantly. Measurement of the modulus in the plateau region between the glass transition of the two polymers is particularly effective because the modulus of the continuous phase contributes more to the multiphase system modulus than the discontinuous phase per unit volume.

2.6 Blend morphology

The word morphology is used in many fields of science. In biology, geology, mineralogy and also in linguistics, it is the science of shapes or structure. The term morphology, when used in the field of polymer, has two meanings, just as in other fields. It means both the science of the supermolecular structure of polymers and also the structure of the polymer material itself, in other words, such structure configurations are visible under the microscope, whether optical or electron. For polymer blends, this term usually uses in the second meaning.

The mechanical properties is directly dependent upon the important macroscopic properties of the material and the morphological arrangement of the polymer materials such as rigidity, strength, brittleness, toughness, long-term stability and others.

In multiphase polymer blend, it is useful to recall the difference between component and phase in blend. A component is an independent chemical individual while a phase is a spatially separate area characterized by a structure arrangement.

In many instances, phase-separated blends are preferred for achieving useful results, such as a polymer-polymer blend may yield materials whose stiffness can be adjusted to any value between those of the component polymers. However, tailoring blends to achieve this or other characteristics requires control over the spatial arrangement or morphology of the phases and some degree of stability once formed. Their arrangement may consist of one phase dispersed as simple spheres in a matrix of the other polymer, as shown in Figure 2.15 (a). On the other hand, dispersed phase may take the form of platelets or fibrils with varying aspect ratio, as shown in Figure 2.15 (b) and 2.15 (c) respectively.

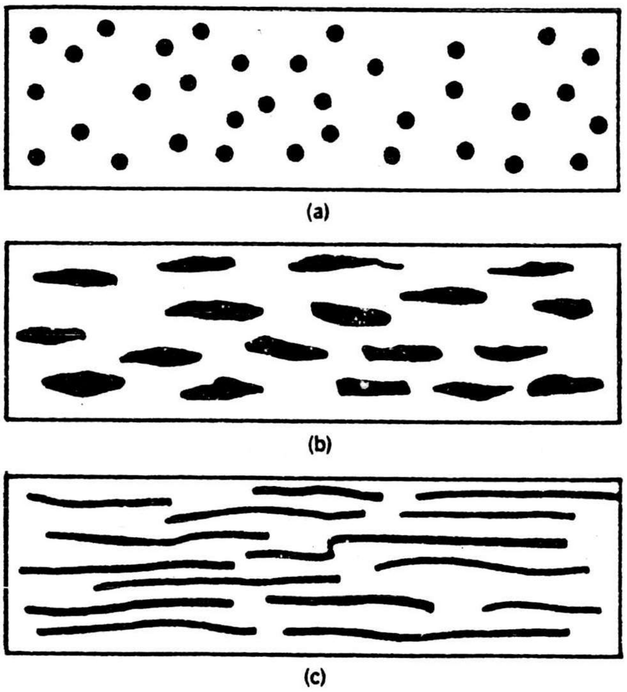


Figure 2.15: Different types of dispersion of a polymer (dark regions) in the matrix of an immiscible polymer. The spherical droplets (a) are progressively extended into platelets (biaxial) (b) or fibrils (uniaxial) (c) by deformation.

These morphological phase arrangements form the three-dimension morphology arrangement known as (a) globular, (b) acicular, (c) rod-like and (d) lamellar, as shown in Figure 2.16.

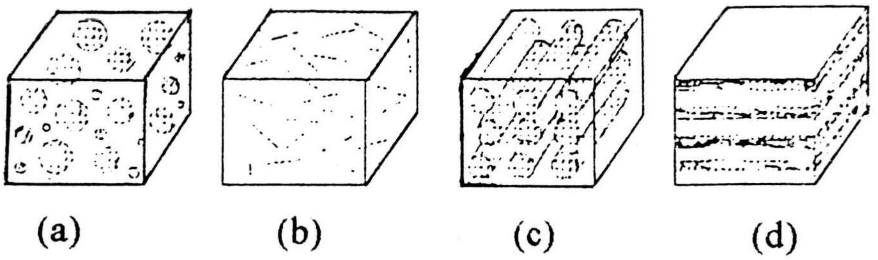


Figure 2.16: Various possibilities for morphological phase arrangement in polymer composites and blends: (a) globular (b) acicular (c) rod-like and (d) lamellar.

Another distinct morphology consists of both phases simultaneously having a continuous character or an interpenetrating network of phases as illustrated in Figure 2.17. Typical dimensions of the phases are important in all these morphologies.

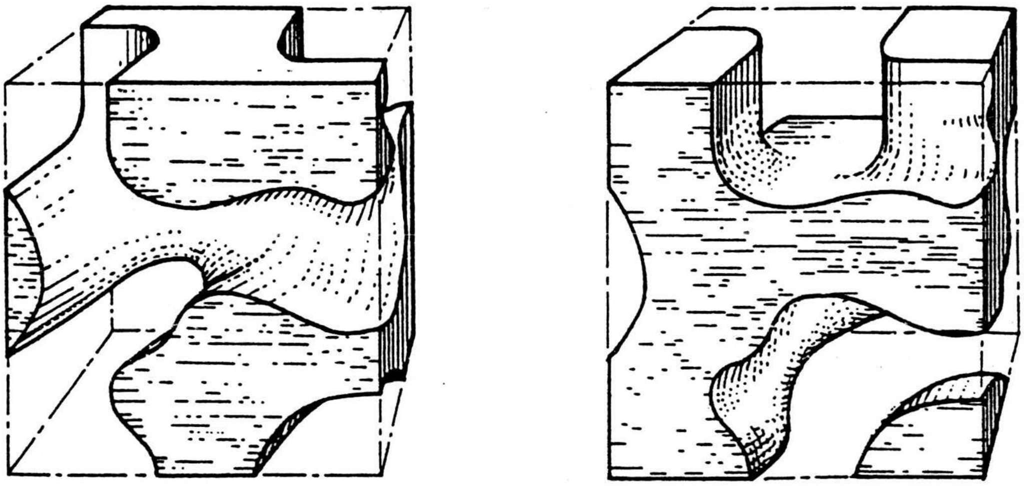


Figure 2.17: Conceptual illustration of interpenetrating network of phases by showing the two interlocking material separated from one another.

2.6.1 Morphology generation and control

Blend composition, viscoelastic properties of the component, interfacial adhesion and the intensity of mixing are parameters known to control the size and the morphology of the dispersed phase and its stability to coalescence.

Melt of two-phase materials are usually mixed continuously in single-screw or twin-screw extruders or they are mixed batchwise in banbury mixers. The morphology generated during mixing depends on the interfacial tension between the phases, the viscosity and the elasticity. The component occupying the most space tends to assume the role of the continuous phase. The size of the dispersed phase is determined by the drop breakup and coalescence, which are governed by the deformation field imposed by the mixing device, the interfacial tension and the rheological characteristics of the component.

The shape of the dispersed phase may be deformed from spheres into fibrils by uniaxial elongational flow, e.g. extrusion through a die, or into platelets by biaxial stretching, e.g. blow molding as shown in Figure 2.15.

The component with the lower viscosity tends to encapsulate the more viscous (or more elastic) component during mixing since this reduces the rate of energy dissipation. Thus the viscosities may be offset by the proportion of the component to control which phase is continuous.

The morphology created during processing is a dynamic structure that may be subject to further changes during subsequent processing step. Block copolymer acts as stabilizers against such changes and as emulsifiers for blends; they are referred to as compatibilizers.

2.7 Process

In melt mixing operation of a polymer blend, the main aim is dispersive mixing in a liquid-liquid system. The differentiation between the distributive and the dispersive mixing is that the distributive mixing is in the majority of the blending operation. The individual component does not influence each other's length scales and mixing is applied merely to randomize the component distribution. The dispersive mixing is the mixing operation involves processes in which one group of components is used to change the length scale of the other to desired level. The polymer blend system, which is initially a two-phase system, is deformed by stress distribution until a desired structure is obtained in such system. As structures in molten polymer systems are difficult to visualize in situ, it is worthwhile to know a priori the relation between the applied stresses and the resulting morphology. Hence, the characterization of the system is necessary.

The systems can be characterized by properties of the components, such as viscosities and elasticities, and system parameters such as interfacial tension, interdiffusion rate and mutual solubility. On the basis of mutual solubility, miscible and immiscible systems can be resolved. Immiscible systems exhibit a considerable interfacial tension and low mutual solubility whereas miscible systems have, in general, zero interfacial tension and infinite mutual solubility. It may be evident that these two cases are only extremes between which actual systems are situated since, especially in polymeric materials, partial miscibility is commonly encountered.

Before blending operation can be initiated, the components must be brought together. In polymer blending, the initial structure is commonly formed by well-stirred granules. After heating the system to temperature above the melt temperatures of both components, applied stresses result in deformation of the structure.

This deformation induces an increase in the interfacial area and it is counteracted by the interfacial tension. However, this interfacial tension induces forces that are reciprocal with the system's length scale and therefore negligible in the early stage of the blending process. This causes the granules to be deformed into long slender bodies when the total deformation is sufficient.

2.8 Compatibilization

The inherent proclivity of high polymers is to form immiscible blends. The physical and mechanical properties of such blends are limited by the large domain size, poor interfacial adhesion and their tendency to form unstable morphologies. So the presence of an interfacial agent of chemical bonds stabilizes the morphology and increases the interfacial adhesion. This is called compatibilization.

Compatibility is enhanced by molecular interactions on the phase contact surface[5]. Their diverse nature is illustrated in Figure 2.18.

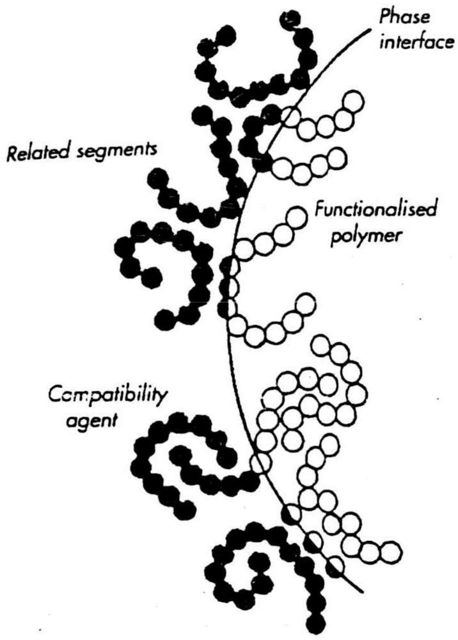


Figure 2.18: Molecular interaction on the phase contact surface.

Compatibility of phases in polymer blends is provided by the local penetration of segments of macromolecular chains or is achieved by the targeted addition of compatibility agents or by chemical modification of the polymer chains. The black and white circles denote units of the different components in the blend. Their interfacial affinity is increased by the presence of compatibilizers concentrating along the interface. These contain units of both types in a single molecule and may be both macromolecular and low-molecular weight substance.

One possibility is the mutual penetration of similar polarity segments of the two types of polymer. Another possibility is the connection of the phases by means of chemical bonds in the block and grafted copolymer. Therefore, one of the way to compatibilize is to functionalize the inert chain. Reactive, polar functional groups are built into the molecule of one of the polymers, which is capable of interacting with hydrogen bridges or of reacting chemically with the molecules of other polymer. Another possibility is to add a third component to the blend, a compatibilizer. This is a low-molecular weight substance or a macromolecular substance which contains two types of chemical groups in a single molecule, while each of them has affinity with one phase of the blend. The compatibilizer is then the intermediate between the two phases. The differences between miscible, immiscible and compatibilized blend are illustrated in Figure 2.19.

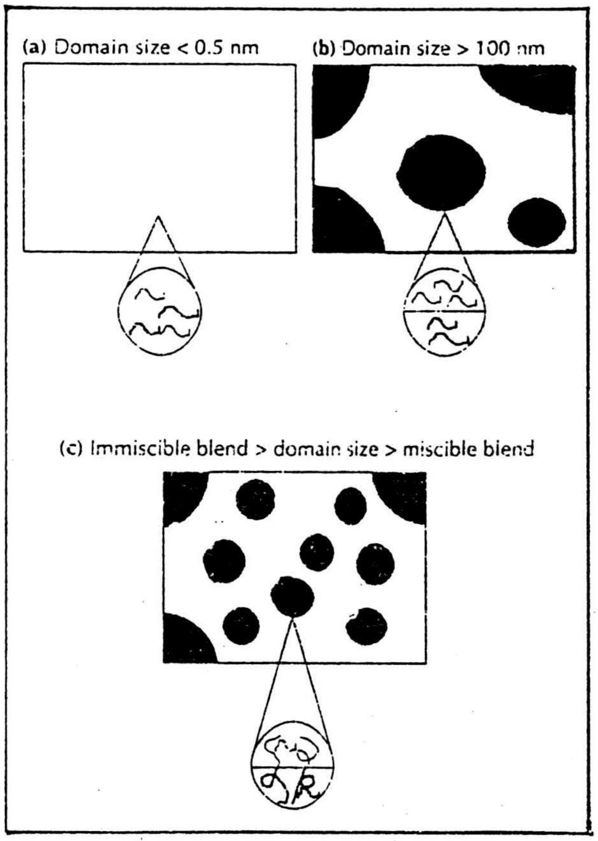


Figure 2.19 Schematic of phase size in (a) miscible (b) immiscible and (c) compatibilized polymer blends.

The compatibilizer are added in partially miscible and immiscible polymer blend in order to

1. reduce the interfacial tension in melt blend which results in the reduction of the phase size.
2. improve the interfacial adhesion and helps distributing the stress at the interface.
3. improve the stability of the distributed phase during quenching/ annealing.
4. upgrade mechanical properties in general.

2.8.1 Types and characteristics of compatibilizing reaction

Compatibilizing reaction in continuous processing equipment usually involves highly reactive functional groups that are stable under the processing conditions. The reaction should be fast and irreversible. In a recent review of reactive compounding in twin-screw extruders, it has been suggested that reactions should be completed within a reasonable period of time (few seconds to about 20 minutes), and be accompanied by low exotherm. Also, the extruder should be able to handle a variety of reactant feeds at various locations along the barrel and be equipped with vents for volatile removal. Knowledge of the reaction kinetics, particularly in a viscous molten polymeric medium, are of paramount importance for the selection of extrusion conditions and the geometry in order to vary the residence times and optimize mixing. Reaction conditions between functionalized polymers may differ considerably from those of low molecular weight (MW) components. A better understanding of the reaction characteristics can often be obtained in batch laboratory mixers or small extruders.

Figure 2.20 contains examples of some important compatibilizing reaction that can take place easily across polymer phase boundaries as will be discussed in more detail later. In addition to the free radical involved in hybridization through recombination reactions, functional groups such as epoxy, anhydride, isocyanate, oxazoline etc., are also highly reactive and meet the above requirements for reaction to be conducted in continuous processing equipment. In addition to covalent reaction, Figure 2.20 contains an example of an ionic reaction leading to the formation of a compatibilizing interchain sulfonate zinc salt.

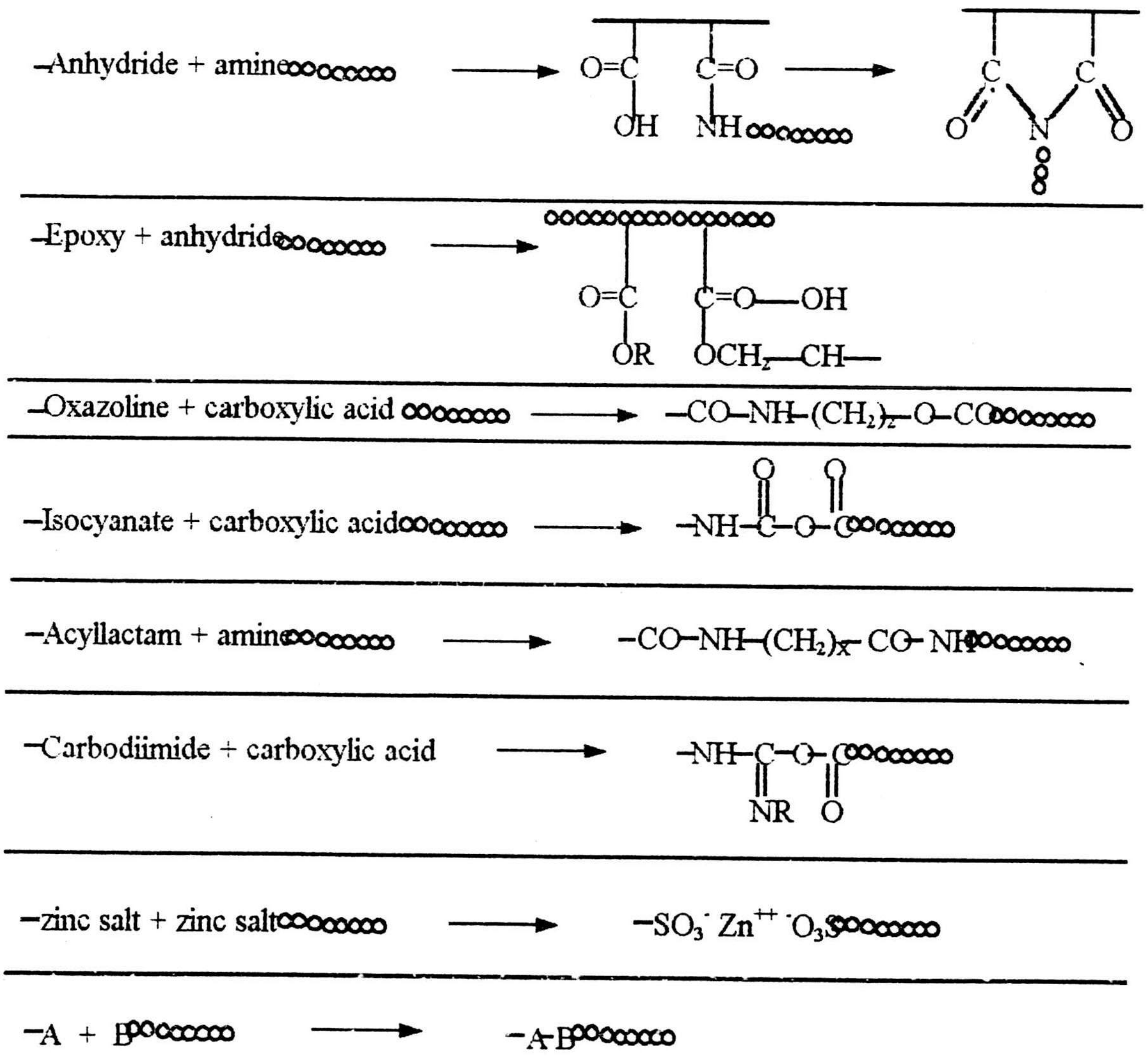


Figure 2.20: Examples of common compatibilizing reactions between functionalized blend constituents.

2.8.2 Routes to reactive compatibilization

2.8.2.1 Functionalized blend components

During melt blending of a pair of suitably functionalized polymers A and B, interchain block or graft copolymers may be formed at various concentrations through covalent or ionic bonding. The *in situ* formed compatibilizers have segments that are chemically identical to those in the respective unreacted homopolymers and are thought to be located preferentially at the interface and thus lowering the interfacial tension. It also promotes mechanical interlocking through entanglements. Table 2.4 illustrates examples on reaction between various functionalized polymers in the absence of any other catalytical acting compounds [6].

Table 2.4: Compatibilization through the reaction functionalized blend components.

Compatibilizing Reaction	Polymer Blend
Anhydride or carboxyl/Amine	PP-g-MA / PA6
	PP-g-AA / PA6
	EAA / PA6
	EPM-g-MA / PA6
	SMA or PS-g-MA / PA6
	ABS-g-MA / PA6
	SEBS-g-MA / PA6
	PPE-g-MA/PA6,6
	Photooxidized LDPE / PA6
	PA6 / Ethylene-acrylic ester-MA terpolymer
Epoxy / Anhydride or carboxyl	(PPE + SMA) / EVA-co-GMA
	PBT / Ethylene-acrylic ester-GMA terpolymer
Oxazoline / Carboxyl	OPS / EAA
Isocyanate / Hydroxyl or Carboxyl	PBT / PCL (isocyanate terminated)
Acyllactam / Amine	EPM-g-acyllactam / PA6
Carbodimide / Carboxyl	PBT / PPE (corbodiimide functionalized)
Transesterification	PC / PBT
	PC / PAR
	PC / Phenoxy

2.8.2.2 Polymeric compatibilizers

Polymeric compatibilizers are reactive copolymers or functionalized polymers of the type A-C (where C is a long reactive segment or a functional group attached to the main chain); they may compatibilize a polymer pair A and B provided that C is capable of chemically reacting with B. In the examples shown in Table 2.5, the non-reactive segment of the polymeric compatibilizer often has different chemical and structural identity from component A, but is still capable of specific interactions leading to a certain degree of miscibility.

Table 2.5: Compatibilization through reactive copolymers functionalized polymers added separately.

Compatibilizing Reaction	Polymer Blend	Polymeric Compatibilizer
Anhydride or carboxyl/Amine	PP or PE or EPM/ PA6 or PA66	PP-g-MA, PP-g-AA, EAA, EPM-g-MA, ionomers
	ABS/PA6	PMMA-g-(carboxyl modified acrylic)
	ABS/(PA6-co-PA6,6)	SAN-co-MA
	PA6/Acrylate rubber (hydroxyl modified)	SMA
	PPE/PA6,6 or PA6	SEBS-g-MA
	PPE/PA6,6	EPM-g-MA + epoxidized EVA
	PBT/PA6,6	PS-co-MA-co-GMA
Oxazoline/Carboxyl	PPE/EAA	OPS
Epoxy/Carboxyl or hydroxyl or anhydride or amine	PPE/PBT	PS-g-(epoxy modified PS)
	NR/PE	PE-g-MA/ENR
	PBT/PA6	PCL-co-S-co-GMA
Interchain salt formation	(PA + PPE)/ Sulfonated EPDM zinc salt	Sulfonated PS zinc salt
	(PS + PPE)/ EPM-g-diethyvinyl phosphonate	Sulfonated PS zinc salt & zinc stearate

2.8.2.3 Low MW compatibilizing compounds

The addition of low MW compounds in a polymer blend may promote compatibilization through the formation of copolymers (random, block, graft) or though the combined effects of copolymer formation and cross-linking, as shown in Tables 2.6 and 2.7. Low MW compounds are usually added at relatively low concentrations (typically 0.1 to 3 %wt); thus, they may offer economic advantages against polymeric compatibilizers that are usually effective at higher concentration.

Table 2.6: Compatibilization through Low MW reactive compounds promoting copolymer formation.

Compatibilizing Mechanism	Polymer Blend	Low MW Compounds
Copolymer formation (block, graft, random)	PET/PA6,6	p-toluene sulfonic acid
	PA6/PA6,6	triphenyl phosphite
	PS-co-VBA/LLDPE	peroxide + coagent
	PMMA/Acrylic	peroxide
	PVC/PP	bismaleimide
	PPE/PA6,6 PC/Polyamide aromatic PE-g-MA/polyester amorphous PBT/MBS	organofunctional silanes (epoxy, amino, vinyl, isocyanate, etc.)
	PBT/EPDM-g-fumaric acid	oligomers (polyamides or polyalkylene oxides)
	SMA/BIIR	dimethylaminoethanol
	POM/Acrylic	organofunctional titanate

Table 2.7: Compatibilization through Low MW reactive compounds promoting copolymer formation and cross-linking reactions.

Compatibilizing Mechanism	Polymer Blend	Low MW Compounds
One phase x-linked/ copolymer formation	PE/PP	peroxide
	EVA or HDPE/ EVACO	EVACO CURATIVES
	PP/NR	peroxide, bismaleimides
	PP or PE/IIR	PF + curatives
	PP/NBR	dimethylol phenolic derivative
	PP/EPDM	rubber curvatives, peroxide
	PA6/NBR	dimethylol phenolic derivative
	PA6/NR	PF + hexa + curvatives
	PVC/PE	Peroxide + triazine dithiol or TAIC + MgO
Both phases x-linked/ copolymer formation	PS/EPDM	Lewis acids
	Rubber/Rubber	commom curvatives
	NR/LDPE	peroxide and coagents
	FPN/NBR or CHR	triazine dithiol complex

2.9 Literature survey

There are very few literature on the compatibilization between polyamide and styrenic polymer via the melt mixing process. M. J. Sullivan and R. A. Weiss [7] studied the improved compatibility of the blends of polystyrene and an amorphous polyamide by using lightly sulfonating the polystyrene. They found that the hydrogen bonding between the amide groups and either the sulfonic acid or the metal sulfonate groups could lower the interfacial tension between the two polymers. As a result, a much finer dispersed phase was observed in the blends involving the sulfonated polystyrene.

A. Molnar and A. Eisenberg [8] studied the miscibility of Polyamide 6 with Lithium or sodium sulfonated Polystyrene ionomers. They prepared the blend of 50/50 w/w of polyamide 6 (PA6) with sulfonated polystyrene ionomers containing 9.8 mol % of functional groups. Single glass transition was found at some compositions, hence the blend was miscible. Considerable miscibility enhancement was observed at certain composition when the counterion was Li^+. The blend system was immiscible when the counterion was Na^+.

Cheng Chung Cheng [9] investigated the instability of phase morphology in blends of polyamides with polyethylenes and polystyrenes and the effects of "compatibilizing" agents on the blends. Styrene-maleic anhydride copolymer was found a more effective compatibilizing agent than styrene acrylonitrile copolymer.

Triacca *et al* [10] studied the melt blends of polyamide 6 with various acrylonitrile-butadiene-styrene terpolymer (ABS). The styrene/acrylonitrile ratio, the content of SAN in the SAN matrix component were examined for rheological behavior, mechanical properties and phase morphology. The blends were found to have poor mechanical properties unless they were properly compatibilized. Modifications was done by adding to the SAN phase a polymer that was miscible with SAN but it must contain functional groups that could react with the polyamide 6 to form *in situ* graft copolymers at the polymer-polymer interfaces. These compatibilizer molecules contained either anhydride or oxazoline units for reactivity.

Yuji Aoki *et al* [11] found the melting point of the polyamide crystallites and the glass transition temperatures of poly (acrylonitrile-co-styrene) (AS), the rubber phase in ABS and the amorphous phase in polyamide to be almost independent of the composition. Their finding suggested that the polyamide and the modified ABS were not mixed at a molecular level although there must have been some interaction between the two polymers.

Polyamide 6/ABS blends compatibilized with imidized acrylic polymer was studied by B. Majumdar, H. Keskkula and D. R. Paul [12]. Reactive polyamide blends with SEBS-g-MA (a maleated styrenic triblock copolymer with ethylene-butylene midblocks), EPR-g-MA (a maleated ethylene/propylene rubber) and ABS were studied in their investigation. Blends of SEBS-g-MA with the mono-functional polyamide 6 led to rubber particles that were too small for toughening upon processing with either a single screw or a co-rotating twin-screw extruder.

M. J. Modic and L. A. Pottick [13] studied the styrenic block copolymers (styrene-ethylene/butylene-styrene) functionalized with maleic anhydride and found that they were useful impact modifiers and compatibilizers for blends of engineering thermoplastics. The paper focused on the use of these functionalized elastomers to modify polyamide 6. At certain compositions, a polyamide material with unique mechanical performance may be achieved by using the functionalized elastomer either alone or in combination with an unfunctionalized styrenic block copolymer.

A. J. Oshinski *et al* [14] studied the combinations of the SEBS and SEBS-g-MA elastomer blends with polyamide 6 and found that a higher level of toughening was achieved than with the functionalized elastomer alone. The particles of pure SEBS were about 5 µm in diameter; this was too large for toughening polyamide 6. SEBS-g-MA alone yielded particles of about 0.05 µm which was too small for optimal toughening. A combinations of the two types of elastomers gave a continuously varying particle size between these extreme limits.