

CHAPTER I

INTRODUCTION

The development of a new blend or compound from existing materials is generally more rapid than a development of an entirely new polymer (Miles and Rostami, 1992). Polymer blending is one of the most popular methods used in developing new materials with desired combinations of properties. This is probably the cheapest and fastest route to developing new plastic material (Uptake, 1995). Blending two or more polymers to obtain a unique product suitable for an application has been practiced for decades. Polymer blends have provided an efficient way to fill new requirements for material properties. Blending is done for a variety of reasons including creating materials with enhanced thermal and mechanical behavior. The great majority of useful blends are immiscible, and in these blends, mechanical properties can be optimized by controlling the blend morphology (Sundraraj and Macosko, 1995).

1.1 Basic Thermodynamic of Polymer Blends

When two polymers are blended, by whatever method, the most likely result is a two phase material. The reason why two polymers are not usually miscible becomes apparent from simple thermodynamic considerations. A necessary (but not sufficient) criterion for miscibility is that the free energy of mixing ΔG_m be negative. This is given by

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1.1)$$

where ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing and T the absolute temperature. In terms of lattice theory developed by Flory and Huggins the entropy of mixing is given by

$$\Delta S_m = -R(N_1 \ln\phi_1 + N_2 \ln\phi_2) \quad (1.2)$$

where N_i is the number of moles and ϕ_i the volume fraction of component i and R is the universal gas constant. The enthalpy of mixing is given by

$$\Delta H_m = RT\chi_{12}N_1\phi_2 = BV_1N_1\phi_2 = (v_1+v_2)B\phi_1\phi_2 \quad (1.3)$$

where v_1 and v_2 are the actual volumes of the components, V_1 is the molar volume of component 1, B is an interaction energy density and χ_{12} is the interaction parameter. The Flory-Huggins χ_{12} parameter is the most important parameter widely used quantities in characterizing a variety of polymer-solvent and polymer-polymer interactions. It is a unitless number (Sperling, 1993) which can be expressed as (Walsh, 1990)

$$\chi_{12} = BV_1/RT = z\Delta w_{12}N_A/RT \quad (1.4)$$

where N_A is Avogadro's number, z is the coordination number of the lattice and Δw_{12} is the energy for the formation of an unlike contact pair which can be expressed as

$$\Delta w_{12} = w_{12} - 1/2(w_{11} + w_{22}) \quad (1.5)$$

where w_{12} , w_{11} and w_{22} are the energies of the respective pair interactions.

We now consider the entropy of mixing as expressed in equation (1.2). As the molecular weight of the polymers in the blends becomes high then the number of moles in the blend, N_1 and N_2 , will become very small. As the molecular weights tend to infinity the number of moles tends to zero and therefore so does the entropy of mixing. Since the entropy of mixing is very small and the enthalpy of mixing is expected to be unfavorable, polymers are not expected to mix.

Mixing can be predicted to occur under three circumstances. (a) If the polymers are not of very high molecular weight then the entropy will not be negligible and may outweigh an unfavorable enthalpy of mixing. Thus one might expect some oligomer mixtures to be homogeneous. (b) If the enthalpy of mixing is positive but very small, then a small entropy of mixing may be sufficient. This might occur if the two polymers are very similar physically and chemically. Thus, for example, copolymers of very similar compositions might be expected to be miscible. (c) If the enthalpy of mixing is negative then two polymers would be expected to be miscible. This might occur if, for example, there is a favorable interaction such as a hydrogen bond between the polymers (Walsh, 1990).

1.2 Polymer Blends

Polymer blends are mixtures of two or more polymers. Polymer blends can be divided into two major categories based on their thermodynamic phase behavior: as shown in **Figure 1.1**.

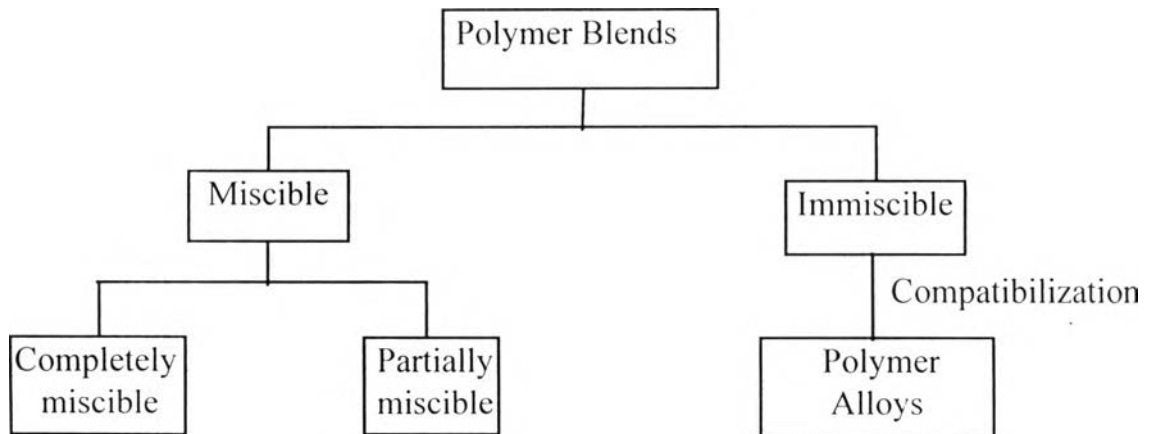


Figure 1.1 Interrelation in polymer blends nomenclature.

The term ‘completely miscible’ is used to describe those blends which are homogeneous at a molecular level. An example of this is the blends of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) with the trade name Noryl. Blends that are homogeneous at some temperatures and phase separate in other accessible temperature regions are referred to as partially or nearly miscible blends. An examples of these blends are the blends of polystyrene with poly(vinyl methyl ether), poly(ethylene oxide) with polyethersulphone and phenoxy resin with polyethersulphone (Rostami, 1992). For immiscible blends, a modification of interfacial properties by compatibilization will lead to the creation of polymer alloys.

1.2.1 Miscible Blends

1.2.1.1 Miscibility. If polymers of a blend are miscible, mixture exists as a single phase which exhibits a single glass transition temperature. The following condition must be satisfied before this can occur :

$$\Delta G_m = \Delta H_m - T\Delta S_m \leq 0 \quad (1.6)$$

where ΔG_m , ΔH_m and ΔS_m are the free energy, enthalpy and entropy of mixing. The entropy of mixing of polymer is very low; therefore, it would virtually be required that the enthalpy of mixing ΔH_m be zero or negative for miscibility (Coran, 1997).

Equation (1.6) implies that exothermic mixtures ($\Delta H_m < 0$) and athermal mixtures ($\Delta H_m = 0$) will mix spontaneously, while for endothermic mixtures ($\Delta H_m > 0$) miscibility will occur at high temperatures (Folkes and Hope, 1993).

1.2.1.2 Partial Miscibility and Phase Diagrams. Many polymers show a variation in miscibility with temperature. Low molecular weight polymers, having large favorable entropies of mixing and unfavorable enthalpies of mixing, are typically more miscible at higher temperatures and may phase separate on cooling, showing upper critical solution temperature behavior (UCST). High molecular weight polymers which form homogeneous mixtures are typically less miscible at higher temperatures and may phase separate on heating, showing lower critical solution temperature behavior (LCST), as illustrated in **Figure 1.2**.

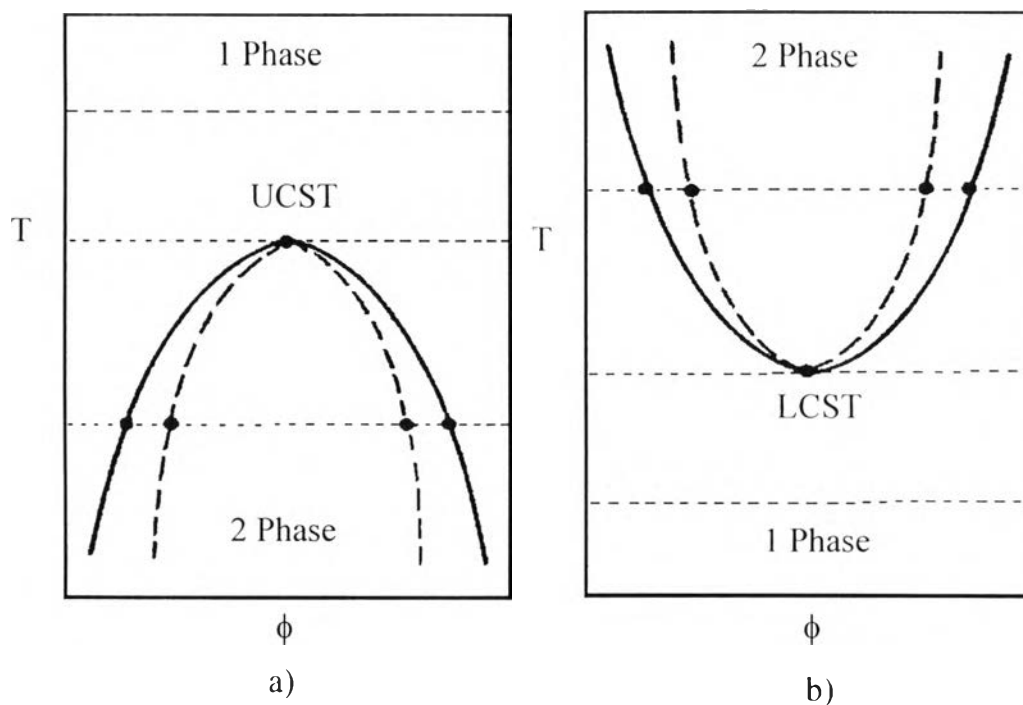


Figure 1.2 Phase diagram for mixtures: (a) upper critical solution temperature (UCST); (b) lower critical solution temperature (LCST).

1.2.2 Immiscible Blends

The thermodynamic condition for immiscible blends is that the Gibbs free energy ΔG_m will be positive (Olabasi, 1979):

$$\Delta G_m = \Delta H_m - T\Delta S_m > 0 \quad (1.7)$$

In the case of immiscible blends, the overall physicomachanical behavior depends critically on two demanding structural parameters: a proper interfacial tension leading to a phase size small enough to allow the material to be considered as macroscopically “homogeneous”, and an interphase

“adhesion” strong enough to assimilate stresses and strains without disruption of the established morphology (Anastasiadis, Gancarz and Koberstein, 1989).

An immiscible mixture of polymers shows multiple phases as determined, for example, by the presence of multiple glass transition temperatures. The thermal transition behavior of immiscible binary mixtures generally reflects the transitions that occur in each nearly pure phase present in the system (Deanin, 1979).

Many immiscible blends exhibit poor mechanical properties because of high interfacial tension, leading to coarse morphology and a lack of interfacial adhesion (Fischer, 1993). The properties of blends can be improved by the addition of small quantity of block copolymers as a “Compatibilizer” that decrease the disperse phase sizes and increase interfacial adhesion (Fischer, 1993, Paul and Newman, 1978).

1.3 Compatibilization

Compatibilization is the process of converting an otherwise useless polymer blends into a commercially useful product.

Compatibilization is important in providing immiscible blends with the morphological stability, processing homogeneity, and interphase interactions required in commercial polymeric materials. In a typical immiscible mixture, the adhesion between the phase is very weak. As a result, physical forces applied to the blend will not be transferred to the dispersed phase, and some properties are significantly lower than would be predicted by the weighted average of the properties of the components. Conversion of these phase separated blends into useful polymeric materials combining the desirable properties of each component requires compatibilization.

Successful compatibilization will reduce interfacial energy, permit finer dispersion during mixing, provide a measure of stability against the development of coarse morphology during the processing /conversion to the final product and result in improved interfacial adhesion. This may be accomplished by (1) the addition of a compatibilizer or (2) changes in the processing conditions. The first approach is of interest here.

Types of compatibilizers may be nonreactive, reactive, or both. The most obvious type of nonreactive compatibilizer is a block copolymer of A and B for a mixture of poly A and poly B, as illustrated in **Figure 1.3**. However, other copolymers may be effective if they have specific interactions, i.e., miscibility, with one or both of the blend components .

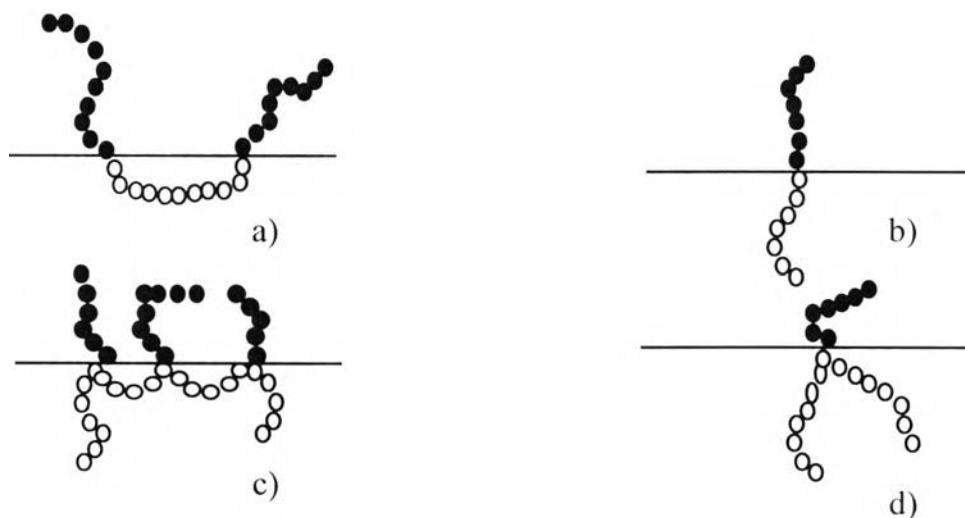


Figure 1.3 Conformations of nonreactive compatibilizers at the interface:
a) triblock copolymer; b) diblock copolymer; c) graft copolymer; d) star-branched copolymer.

Reactive compatibilizers is a polymer that can chemically react with one or both of the phases. It can provide the strength and stability of the blend morphology throughout the processing and service life of the final product.

Included in this type of compatibilizer are the crosslinked or vulcanized blends.

In this study, we shall investigate the triblock copolymer as a nonreactive compatibilizer.

1.4 Block Copolymer

1.4.1 Morphology of Block Copolymers

Block copolymers consist of chain molecules, each of which contains sequences of “soft” and “hard” segments as illustrated in **Figure 1.4**. These are dissimilar and incompatible with each other so that they act as individual phases.

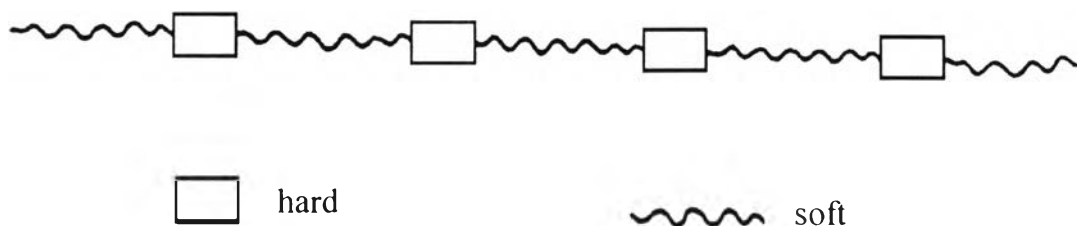


Figure 1.4 A chain molecule of a block copolymer.

The dominant soft segments are flexible, amorphous and have low glass transition temperatures. Conversely, the hard segments have a high melting point and tend to aggregate at ordinary temperatures into rigid domains to form physically effective “pseudo” cross-links, as illustrated in **Figure 1.5**.

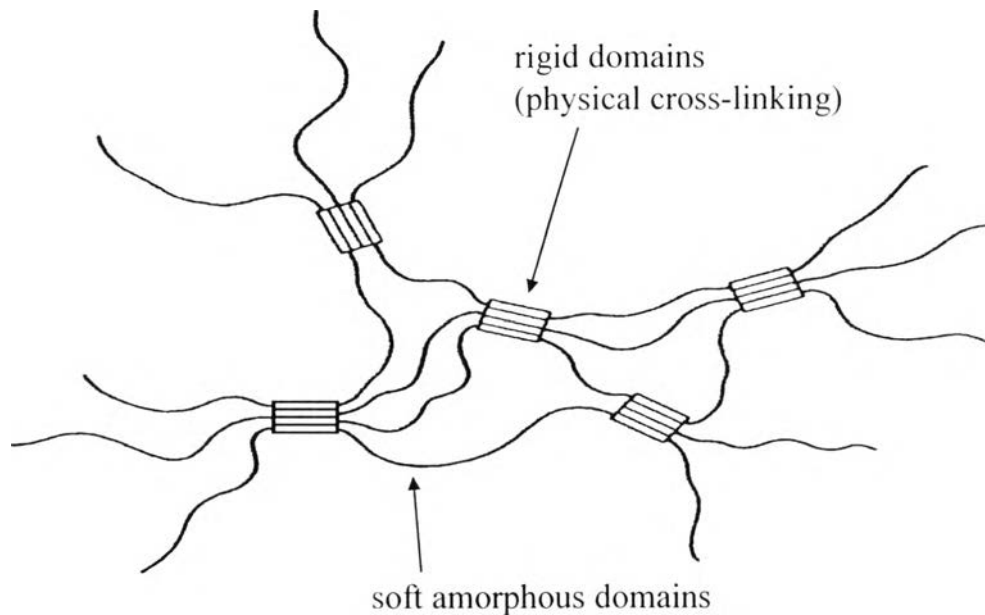


Figure 1.5 Morphology of block copolymer.

When the block copolymer is heated, the forces that bind the hard segments together will be destroyed. On cooling, the hard segments reassociate into rigid domains and the material shows elastomeric properties once again.

Suitable solvents are able to destroy the pseudo cross-links. When the solvent is evaporated, the hard segments reassociate into rigid domains (Miles and Rostami, 1992).

1.4.2 Block or Graft Copolymer As a Compatibilizer for Immiscible Blends

When two homopolymers A and B are immiscible, they exhibit a high interfacial tension that leads to low interfacial adhesion, and to stable disperse phase particles of large sizes and wide size distribution (Adedeji, Hudson and Jamieson, 1996). Interfacial tension is the single most accessible experimental parameter that describes the thermodynamic state and structure

of an interface. Moreover, interfacial tension is very important directly to the mechanical properties of the immiscible polymer blends (Jo, Nam and Cho, 1996). A simplest way to lower the interfacial tension and to improve the interfacial adhesion between the phases is to add a block or graft copolymer (a so called compatibilizer) (Eastmond, 1987). The copolymer will migrate to the interface and compatibilize the phase separated-blends. Thus, the compatibilizer behaves as a classical emulsifying agent similar to soap molecules at an oil-water interface (Inuo, Soen, Hashimoto and Kawai, 1970). The use of a compatibilizer as a surfactant in immiscible blends can dramatically improve mechanical and morphology properties.

The model studies have frequently been performed on miscibility of binary blends consisting of a homopolymer A with a block copolymer A-b-B, which has one segment of similar chemistry to that of the homopolymer (i.e., A/A-b-B isochemical blends) (Adedeji, Jamieson and Hudson, 1995). For ternary blends consisting of two homopolymers A and B in the presence of an A-b-B block copolymer. The effective solubilization requires that the molecular weight of the homopolymers be less than or equal to that of the block copolymer (Akiyama and Jamieson, 1992). In this study, we examined polystyrene/poly(styrene-b-isoprene-b-styrene)/polyisoprene ternary blends (i.e., PS/P(S-b-I-b-S)/PI).

Another model is the blends with a block copolymer whose segments are chemically different from the homopolymer (A/X-b-B or A/X-b-B/B), but one of the segments (X) has a specific exothermic interaction with the homopolymer (Adedeji, Jamieson and Hudson, 1995). This case should also work well to improve interfacial adhesion and blends properties. In this study, we examined poly(2,6-dimethyl-1,4-phenylene oxide)/poly(styrene-b-isoprene-b-styrene)/polyisoprene ternary blends (i.e., PPO/P(S-b-I-b-S)/PI).

1.5 Literature Survey

Several theoretical and experimental studies on the interfacial activity of a block copolymer in immiscible polymer blends have been reported. It has been found experimentally (Jo et al., 1996, Hu et al., 1995, Anastasiadis et al., 1989, Noolandi and Hong, 1982, and Patterson et al., 1971) that the interfacial tension decreases with increasing concentration of block copolymers and that block copolymer micelles are formed when the copolymer concentration in the homopolymer phase exceeds the critical micelle concentration (CMC).

Jo, Nam, and Cho (1996) studied the effect of the molecular structure of the styrene-isoprene block copolymer on the interfacial tension, the morphology and the interfacial adhesion of polystyrene/polyisoprene. A reduction in interfacial tension was observed with the addition of a small amount of copolymer, followed by a leveling off as the copolymer concentration exceeds the critical micelle concentration. The result showed that the reduction of interfacial tension between polystyrene and polyisoprene is more significant when symmetric or styrene-rich diblock copolymer is added. The interfacial tension data seem to be consistent with the phase morphology and the interfacial adhesion.

Hu, Koberstein, Liniger and Gallot (1995) studied interfacial tension reduction in polystyrene/poly(dimethylsiloxane) blends by addition of poly(styrene-*b*-dimethylsiloxane). They examined the ternary system comprising polystyrene (PS), poly(dimethylsiloxane) (PDMS), and poly(styrene-*b*-dimethylsiloxane) [P(S-*b*-DMS)]. The interfacial tension was measured by using an automated pendant drop tensiometer. They found that the interfacial tension of the blend initially decreased upon an increase in the copolymer concentration and then attained a constant value above a certain critical copolymer concentration (0.002%).

Anastasiadis et al. (1989) used an automated pendant drop apparatus to study the compatibilizing effect of block copolymer addition on the interfacial tension between two immiscible homopolymers. They investigated the ternary system polystyrene/1,2-polybutadiene/poly(styrene-*block*-1,2-butadiene) as a function of copolymer concentration. A sharp decrease in interfacial tension was observed with addition of a small amount of copolymer (40% reduction with 1.29% additive), followed by a leveling off as the copolymer concentration is increased (50% total reduction with 3.5% copolymer) above the apparent of critical micelle concentration (CMC). The leveling off at higher concentrations indicated the interfacial saturation by the copolymer and subsequent formation of copolymer micelles dispersed in the homopolymer phases. They also found that an estimate of the critical micelle concentration (CMC) was 1.6 grams of copolymer per gram of polystyrene. For concentrations below this critical concentration, the interfacial tension reduction was essentially linear in the copolymer content and compare well with the predictions of Noolandi and Hong.

Noolandi and Hong (1982) studied theoretically the interfacial properties of block copolymers in immiscible homopolymer blends by using a general formalism for inhomogeneous multicomponent polymer systems. They found that the interfacial tension was reduced with increasing block copolymer concentrations for a range of copolymer and homopolymer molecular weights. They pointed out that both copolymer concentration and molecular weight are equally important in reducing the interfacial tension. The theory of Noolandi and Hong holds for highly incompatible systems. For concentrations below the CMC, interfacial tension was expected to decrease linearly with copolymer concentration, whereas for concentrations higher than the CMC a leveling off was expected.

Patterson et al. (1971) used a rotating drop apparatus to study the effect of addition of poly(dimethylsiloxane-*block*-oxymethylene) copolymers on the interfacial tension between methyl terminated poly(dimethylsiloxane) and a poly(oxyethylene-*block*-oxypropylene) copolymer. They found that the interfacial tension was reduced by 72% with the addition of 2% of a 60/40 poly(dimethylsiloxane-*block*-oxyethylene)

The recent literature contains several reports on the effect of exothermic interaction in polymer blends (Adedeji et al., 1996, Ziaee and Paul, 1996, Akiyama and Jamieson, 1992, and Tucker et al., 1988).

Adedeji, Hudson and Jamieson (1996) studied the effect of exothermic interfacial mixing on interfacial activity of a block copolymer. They measured the variation in the exothermic interaction of poly(methyl methacrylate-*b*-styrene) (PMMA-*b*-PS) in solvent-cast blends of poly(styrene-co-acrylonitrile) (SAN) with polystyrene (PS) as a minor component by using transmission electron microscopy (TEM). Three molecular weights of PMMA-*b*-PS (65, 283 and 680) were used. The exothermic mixing between SAN and PMMA and the repulsion between SAN and PS were systematically varied by changing the AN content of the SAN from 15 to 26, 29, and 33%. They found that the degree of incompatibility $N\chi_{\text{SAN-PS}}$, the molecular weight ratio M_h/M_b of PS homopolymer to PS block copolymer segment, and the degree of exothermic mixing between SAN and PMMA were all important in determining the morphology of the disperse phase.

Ziaee and Paul (1996) studied the polymer-polymer interactions via analog calorimetry in blends of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide). They found that the enthalpic interaction energy for the blends of PS-PPO is -1.35 ± 0.19 cal/cm³. These results indicated that electronic rearrangements between the phenyl ring and substituted methyl groups in PPO have a large influence on the interaction with polystyrene.

Akiyama and Jamieson (1992) studied the enthalpic interaction in the copolymer/homopolymer blend systems. They measured morphology of solvent cast films containing a polystyrene/poly(methyl methacrylate) (PS/PMMA) with polystyrene (PS), random styrene acrylonitrile copolymer (SAN) and poly(methyl methacrylate) (PMMA). They found that the morphology of the blends changes systematically from dispersed spheres to cylinder, vesicles and lamellae, depending on the strength of the enthalpic interaction between the matrix and the copolymer segments.

Tucker and Paul (1988) developed a simple model for estimating the effect of enthalpy in homopolymer/block copolymer blends. The model assumes a lamella domain morphology and ignores any interfacial effects. They found that an exothermic interaction dramatically alters the phase behavior from that of an athermal system, e.g., polystyrene homopolymer blends with styrene-based block copolymers. The model predictions are compared with experimental results given in a companion paper (Tucker et al., 1988) for blends of poly(phenylene oxide) with styrene-based block copolymers. The exothermic interaction of this system greatly increases the extent of homopolymer incorporation into the copolymer domains and makes the molecular weight of the homopolymer a relatively unimportant parameter compared to the athermal case.

Tucker, Barlow and Pual (1988) studied the effect of molecular weight on phase behavior of blends of poly(phenylene oxide) with styrenic triblock copolymers. They measured the degree of solubilization of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) homopolymer in the polystyrene (PS) microphase of triblock copolymer by differential scanning calorimetry. They found that the exothermic heat of mixing for PPO and PS units causes a dramatic increase in the extent of homopolymer solubilization. The result showed that the molecular weight of the PS block (from 5,300 to 47,000) is a major factor

determining the extent of PPO and PS segments. While the molecular weight of the PPO has a little or no effect over the range investigated (23,900 to 39,000). Rubber block type, size or location does not appear to have a major effect on solubilization within the limited range examined.

Adedeji, Jamieson and Hudson (1996) studied morphologies of solvent cast ternary isochemical A/A-b-B/B and heterochemical A/X-b-B/B blends by using the transmission electron microscopy. They found that the morphology of such blends is controlled by the delicate balance in the swelling of each block copolymer segment by the corresponding compatible homopolymers. The morphologies of ternary blends of the type A/A-b-B/B and A/X-b-B/A can be related to the phase behavior (for example, the requirement that the molecular weight of the homopolymer (P) be less than or equal to that of the block copolymer (N). in the phase containing similar chemistries, and that the repulsive $N\chi_{AB}$ be sufficiently small) observed in the binary A/A-b-B and A/X-b-B blends

1.6 Objectives

The objectives of this research project are:

- (1) To investigate the effect of exothermic interaction on the effectiveness of the SIS triblock copolymer in compatibilizing two immiscible blends; PS/PI and PPO/PI.
- (2) To study the effect of triblock copolymer on viscoelastic properties of the ternary blends.
- (3) To investigate changes in morphology of the immiscible polymer blends due to the triblock copolymer.