# CHAPTER I

# INTRODUCTION

Development of new molecules and chemical modifications of existing ones are challenging for polymeric materials scientist. These tasks, however, have become increasingly complex and expensive over the years. Thus, an alternative has become more important and attractive. Polymer blending is one such approach that is presently in a state of a rapid scientific development and attractive for commercial purpose. Polymer blends have provided an efficient way to fill new requirements for material properties. Blending can usually be fulfilled more economically than the development of a new chemistry. Blending of thermoplastic polymers can improve mechanical properties such as toughness, and is frequently a method for the development of novel thermoplastic alloys and blends (Folks and Hope, 1993).

## 1.1 Polymer Blends

Polymer blends are mixtures of at least two polymers. Polymer blends can be devided into two major classes based on their thermodynamic phase behavior.

### 1.1.1 Miscible Blends

When two polymers, A and B form a homogeneous mixture, many properties of the blend are additive (Olasbisi, 1979 and Paul, 1980). A thermodynamic condition for miscibility involve an appropriate balance of the enthalpy and entropy terms in the Gibbs free energy of mixing, i.e., the free energy of mixing $\Delta G_{mix}$, must be negative (Olabisi, 1979) :

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}; \tag{1.1}$$

if $$\Delta G_{mix} < 0, \tag{1.2}$$

then $$\Delta H_{mix} - T\Delta S_{mix} < 0, \tag{1.3}$$

where $\Delta H_{mix}$ is the enthalpy of mixing, $\Delta S_{mix}$ is the entropy of mixing and T is temperature. Equation (1.3) implies that exothermic mixtures ($\Delta H_{mix} < 0$) and athermal mixtures ($\Delta H_{mix} = 0$) will mix spontaneously, whereas for endothermic mixtures ($\Delta H_{mix} > 0$) miscibility will only occur at high temperatures ( Folkes and Hope, 1993).

Thus for a miscible blend, the favorable entropic contribution must be large enough to yield a negative free energy of mixing. For the enthalpic part negative, zero or small positive $\Delta H_{mix}$ values are required for miscibility.

### 1.1.2 Immiscible Blends

An immiscible mixture of polymers shows multiple amorphous phase as determined, for example, by presence of multiple glass transition temperatures. A thermodynamic condition for immiscible blends is that the free energy $\Delta G_{mix}$ , will be positive (Olabisi, 1979).

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}, \tag{1.4}$$

where $$\Delta G_{mix} > 0. \tag{1.5}$$

If $\Delta H_{mix}$ is positive, phase separation can occur.

Blends of immiscible polymer have complex property composition that are rarely additive (Olabishi, 1979 and Paul, 1980). Most properties are dramatically influenced by the spatial arrangement of the phases in the final blend. The morphology is strongly affected by processing history and a change in morphology can become undesirable during fabrication steps since it is a dynamic structure.

Properties like stiffness or heat distortion temperature are dominated by the component forming the continuous phase and show a spinoidal shape versus composition owing to the phase inversion (Keitz, 1984 and Shaw, 1982).

The poor mechanical behavior of phase separated blends is usually the consequence of inadequate adhesion between phases that does not allow efficient transfer of stress across the interface. One method to improve the interfacial characteristic of immiscible blend is to add a small quantity of block or graft copolymer as a " Compatibilizer" (Paul and Newman, 1978).

## 1.2 Block or Graft Copolymer as a Compatibilizer for Immiscible Blends

When two homopolymers A and B are immiscible, they exhibit a high interfacial tension, which leads to stable disperse phase particles of large sizes with a broad distribution. Moreover, interfacial tension is very important because it has much to do with the phase morphology and the interfacial adhesion, affecting directly the mechanical properties of the immiscible polymer blends. A simple 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) which has an affinity for both initial polymers. The copolymer will migrate to the interface and compatibilize the phase separated-blend. Thus, the compatibilizer behaves as a classical emulsifying agent similar to soap molecules at an oil-water interface (Inuoe, Soen, Hashimoto and Kawai, 1970). The use of a compatibilizer as a surfactant in immiscible blends can dramatically improve mechanical and morphology properties.

The idea of localisation of block or graft copolymer at polymer-polymer interface is shown in Figure 1.1.

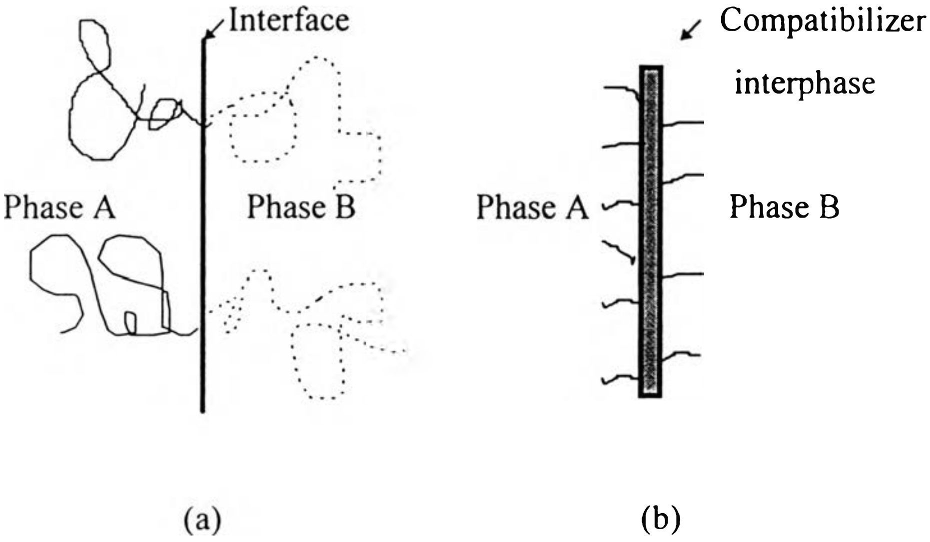

**Figure 1.1** (a) Ideal configuration of a block copolymer at the interface between polymer phases A and B. (b) Formation of an interphase between phases A and B promoted by a compatibilizer.

In its simplest form, the compatibilizer has block or graft segments which are chemically identical to those in the respective phases. Homopolymers A and

B in the presence of an A-b-B diblock copolymer. When the diblock copolymer is added into the system, the entropy of mixing of the block copolymer with the homopolymers favor a random distribution of the copolymer in the bulk. However, the unfavorable interaction between the A and B segments tends to drive the copolymer toward the interface, with the blocks extending into their respective homopolymer phases (i.e., block A in the homopolymer A phase and vice versa). This not only minimizes the contacts between the unlike segments of the diblock copolymer and homopolymer but also displaces the two homopolymers away from the interface, thereby decreasing the enthalpy of mixing between the homopolymers. In this study, we examined polystyrene/poly(styrene-b-isoprene)/polyisoprene ternary blends (i.e., PS/P(S-b-I)/PI ).

Another possibility is nonidentical segments which are miscible in the respective phases. Here homopolymers A and B are mixed with X-b-Y or X-b-B diblock copolymer, and exothermic mixing occurs at the interface (i.e., between A and X ) (Paul and Barlow, 1980). This case should also work well to improve interfacial adhesion and blend properties. In this study, we examined poly(2,6-dimethyl-1,4-phenylene oxide)/poly(styrene-b-isoprene)/polyisoprene ternary blends (i.e., PPO/P(S-b-I)/PI ).

## 1.3 Literature Survey

David, Karen and Edwin (1988) studied the structural transitions from spherical to nonspherical micelles in blends of poly(styrene-butadiene) diblock copolymer and polystyrene homopolymer. This study shows that transitions from micelle shape to mesophase type can occur by increasing the molecular weight of the homopolymer matrix, by increasing the aggregating block molecular weight, or by increasing the volume fraction of the copolymer.

Tucker, Barlow and Paul (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 copolymers by differential scanning calorimetry. They found that the molecular weight of the PS block 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 (23,000 to 39,000). Rubber block type, size or location does not appear to have a major effect on solubilization within the limited range examined.

Balasz and De Meuse (1989) studied the effect of sequence distribution of a copolymer on the miscibility of ternary mixtures which contain a copolymer and two homopolymers. The results show that the sequence distribution of the monomers in copolymer plays an important role in the phase behavior of these ternary blends and that a block copolymer may not be the best thermodynamic compatibilizer in a ternary mixture.

Hu, Koberstein, Lingeber 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%).

Mark Dadmun (1996) studied the effect of copolymer architecture on the interfacial structure and miscibility of a ternary polymer blend containing a copolymer and two homopolymers. These effects were examined by using Monte Carlo Simulation. He found that at low copolymer concentration (Ca. 1%), the phase transition from immiscible to miscible does not change within the resolution of the simulation for any of the copolymer structure studied, which include block, random, and alternating architectures. He showed that both block and alternating structures show promise as interfacial modifiers. While the purely random copolymer has the weakest effect on interfacial strengthening.

Jo, Nam, and Cho (1996) studied the effects of the molecular structure of the styrene-isoprene block copolymer on the interfacial tension, the morphology and the interfacial adhesion of polystyrene/polyisoprene. The results show that the reduction of interfacial tension between polystyrene and polyisoprene is more significant when the isoprene- rich diblock copolymer is added than the case 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.

### 1.4 Research Objectives

To investigate the effect of styrene-b-isoprene block copolymers on mechanical properties of blends of (polystyrene + polyisoprene) and ( poly 2,6-

dimethyl-1,4-phenylene oxide + polyisoprene). By matching molecular weight of PS and PPO. We purpose to evaluate the influence of the exothermic interaction between PS and PPO on polyisoprene.