CHAPTER I

INTRODUCTION

During the past two decades, there has been a lot of progress in the field of polymer blends. Since the properties of polymer blend system are functions of the composition, polymers can easily and quickly be blended to meet performance and cost objectives required by the markets. Blending can usually be fulfilled more economically than the development of a new chemistry. In terms of reducing costs, new polymer blend systems are particularly attractive when one of the components is much less expensive than the others; this allows the polymer blend to be produced at a lower cost than that of the higher cost component (Shaw, 1982, Utracki, 1982 and Robeson, 1984).

In the year 1983, the production of commercial alloys and blends (not including rubber-toughened products such as HIPS and ABS) was 540×10^6 ton or 3 % of the total polymer production (*Chem. Week*, 1983). It is growing at a rate higher than the 10 % growth rate of the entire polymer industry.

1.1 Polymer Blends

In general, the properties of polymer blends depend on a composition weighted average of the properties possessed by the components. However, the properties of the blends also vary in a complex way depending on the nature of the components (glassy, rubbery, or semicrystalline), and the thermodynamic state of the blend (miscible or immiscible).

1.1.1 Miscible Blends

There is only one phase for miscible binary blends of amorphous polymers. The properties of miscible blends are related to those of the blend components. Commercially important examples of these blends are Poly (Phenylene Oxide) (PPO) - Polystyrene (PS) (the 1st miscible blend in the world), PVC-nitrile rubber, and Poly(Vinyl Chloride) (PVC) - Methyl Styrene - Acrylonitrile (MeSAN) blends. The glass transition temperature T_g is the primary thermal transition for these blends, and it varies with the composition ratio of the blends.

For the thermodynamic state of the blend, equilibrium-phase behavior of mixtures is governed by the free energy of mixing

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

consisting of the enthalpic (ΔH) and entropic (ΔS) parts, the former is affected by composition and temperature T. For miscibility (Olabisi, 1979 and MacKnight, 1978), ΔG_{mix} must be negative.

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

Thus for a miscible blend, the favorable entropic contribution must be large enough to yield a negative free-energy of mixing. And for the enthalpic part, exothermic mixing, $\Delta H_{mix} < 0$, is required to guarantee the miscibility of the blend.

1.1.2 Immiscible Blends

An immiscible blend is defined as an immiscible mixture of polymers which shows multiple amorphous phases as determined, for example, by the presence of multiple glass-transition temperatures.

On the thermodynamic state of the immiscible blend, if the endothermic mixing, $\Delta H_{mix} > 0$, is present, the polymer-polymer adhesion will not be good. The free energy of mixing will be positive.

$$\Delta G_{mix} > 0, \tag{1.3}$$

The multiple amorphous phases can give the effect of composition retio on properties different from those of miscible systems. For example, in amorphous immiscible binary blends, the properties of the principle component largely determine the properties of the blend (Keitz, 1984 and Shaw, 1982), as shown in fig. 1.1.

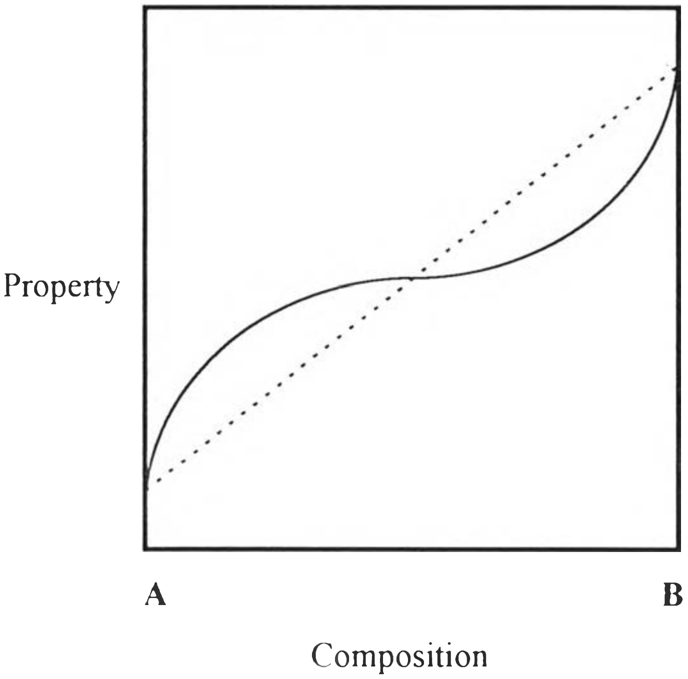

Figure 1.1 Property vs composition profiles of immiscible (——) and miscible (------) blends.

This contrasts with the more nearly linear composition dependence shown for miscible amorphous binary systems and suggests some advantage in forming immiscible blends.

For an immiscible blend, poor elongation and impact strength are related to poor stress transfer between the phases. Since low molecular attractive forces between the blend components are responsible for the immiscible phase behavior, low attractive or adhesive forces between phases are to be expected. It is believed that poor interfacial adhesion causes premature failure under an applied stress as a result of the usual crack-opening mechanisms (Paul, 1978).

1.2 Block Copolymer

Block copolymers of the monomers A and B are formed in sequence arrangements such as -AAAAAAAAAAAAAAA-BBBBBBBBBBBBBB- and -AAAAAAAAAA-BBBBBBBBBB-AAAAAAAAAA-, and the polymers are named, respectively, polyA-*block*-polyB and polyA-*block*-polyB-*block*-polyA. For example, the diblock copolymer of polystyrene and polybutadiene is polystyrene-*block*-polybutadiene or poly(styrene-*b*-butadiene).

The structure of such domains is shown in fig. 1.2. The individual blocks assume nearly random coil conformations within each domain, and the junction between the two blocks is at the interface.

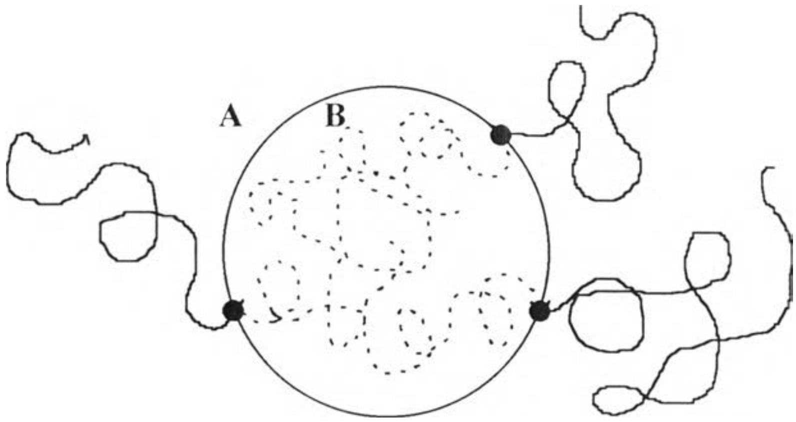

Figure 1.2 The model of a block copolymer domain.

1.3 Block Copolymer as a Compatibilizer for Immiscible Blend

The localization of surfactants at water/oil interfaces can reduce the interfacial tension. There are many previous studies which have shown that block copolymers can act in the same behavior as the surfactant at water/oil interface when added to immiscible polymer blends.

The properties of immiscible blends would be improved if the interfacial interaction could be increased or strengthened by incorporating an interfacially active block or graft copolymer compatibilizer as shown in fig. 1.3.

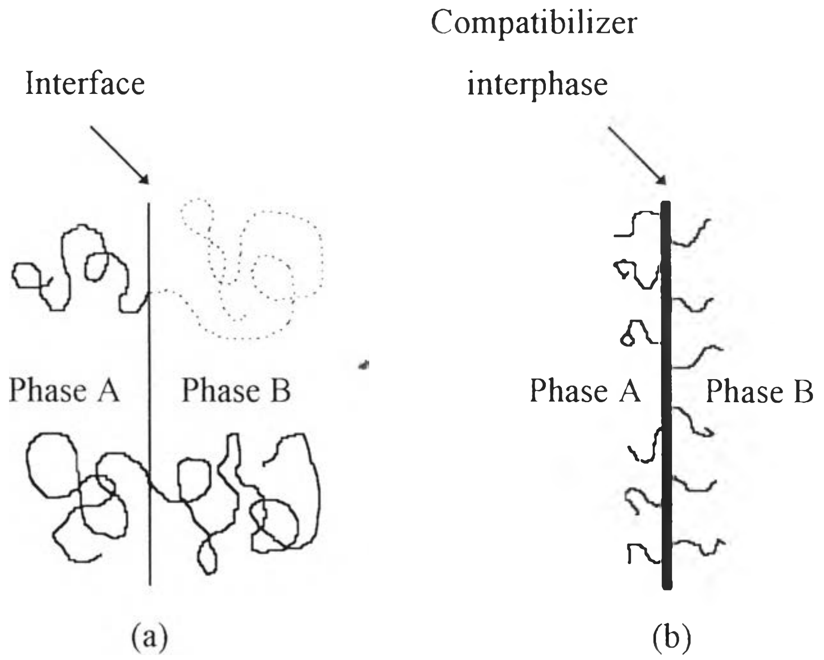

Figure 1.3 (a) Ideal configuration of a block copolymer at the interface between polymer phases A and B. (b) Formation of an interphase between phases A and B promoted by a compatibilizer.

In general, a compatibilizer has block or graft segments that are chemically identical to those in the respective phases. For example, poly (isoprene-*b*-styrene) diblock copolymer can compatibilize immiscible blends of polyisoprene and polystyrene. For nonidentical segments which are miscible or partially miscible in the respective phases, they should also work well to improve interfacial adhesion and blend properties.

1.4 Literature Survey

Bartlett, Barlow, and Paul (1982) studied the composition vs mechanical-property relationships observed in immiscible mixtures of poly (ethylene) (PE) and poly(propylene) (PP), and the benefits provided by compatibilizing copolymers. PE and PP are both tough and ductile homopolymers with similar chemical structures. These materials form brittle immiscible mixtures when melt-blended and compression-molded. The addition of 10-20 wt % of a ethylene-propylene diblock copolymer (Epcar) greatly improves ductility of compression-molded blends, although the modulus and strength are reduced by the addition of the rubbery copolymer.

Fayt, Jerome, and Teyssie (1986) studied the compatibilization of immiscible blends of PE and PS by various hydrogenated butadiene-styrene diblock copolymers. Based on a combination of microscopy and assessment of mechanical-property improvement, it was found that as little as 0.5-2.0 wt % of diblock copolymer is sufficient to achieve a homogeneous and stable phase dispersion. Most of the copolymer is at the interphase and diblock copolymers with blocks of similar size are the most efficient interfacial agents.

Kole, Bhattacharya, Tripathy, and Bhowmick (1993) studied the effect of compatibilizer, silane-grafted EPR, on glass transition and storage modulus of a 50/50 blend of silicone/EPDM. Storage modulus is found to decrease with compatibilizer concentration up to 5 % and then steadily increase with an increased dose of compatibilizer. The specimen having 5 % compatibilizer has the lowest storage modulus followed by the specimen containing 3 % compatibilizer. Silane-grafted EPR acts as a compatibilizer for silicone and EPDM, and can show a good compatibilization only for some optimum concentrations of silane-grafted EPR copolymer.

Sundararaj and Macosko (1995) studied the effects of concentration and compatibilization on drop breakup and coalescence in polymer blends. This study shows that a limiting dispersed phase particle size exists at very low concentrations for polymer blends mixed in an internal batch mixer and two types of twin-screw extruders. In uncompatibilized blends, the final particle size increases with the dispersed phase concentration due to increased coalescence. The particle size distribution also broadens at higher concentrations. Adding diblock copolymers suppresses coalescence resulting in smaller particle size and narrower particle size distribution.

Hu, Koberstein, Lingelser, and Gallot (1995) studied the effects of diblock copolymer addition on the interfacial tension of immiscible homopolymer blends. They examined the ternary system comprising polystyrene (PS), poly(dimethylsiloxane) (PDMS), and poly(styrene-*b*-dimethylsiloxane) [P(S-*b*-DMS)]. They measured interfacial tension by using automated pendant drop tensiometer. The interfacial tension of the blend initially decreases upon an increase in the copolymer concentration and then attains a constant value above a certain critical concentration.

Jannasch, Gunnarsson, and Wesslen (1996) studied the compatibilizing effect of poly(styrene-*graft*-ethylene oxide) (SEO) in polystyrene (PS) and poly(*n*-butyl acrylate-*co*-acrylic acid) (PBAAA). Thermal and dynamic mechanical analysis of the PS/PBAAA blends revealed that the PBAAA glass transition temperature (T_g) decreased with increasing graft copolymer content. The effect of the graft copolymer in the PS/PBAAA blends can be explained by interactions across the interface due to the formation of hydrogen bonds between the poly(ethylene oxide) (PEO) side chains in the graft copolymer and the acrylic acid segments in PBAAA phase.

1.5 Objectives

For this research, polyisoprene (PI) and polystyrene (PS) were used as the homopolymers, and poly(isoprene-1, 4-*b*-styrene) [P(I-*b*-S)] was used as the compatibilizer.

The purposes of this research are three parts: first is to study the effect of composition ratio of immiscible blend on mechanical properties. The second is to study how the block copolymer acts as a compatibilizer for an immiscible system. The third is to examine and find out particular composition ratios of the blend that block copolymer can work effectively.

For the dynamic modulus measurements, the dynamic moduli (loss modulus and storage modulus) were measured as functions of the blend composition and % block copolymer. For the mechanical modulus measurements, the Young's modulus and the strain rate were measured as functions of the blend composition.