

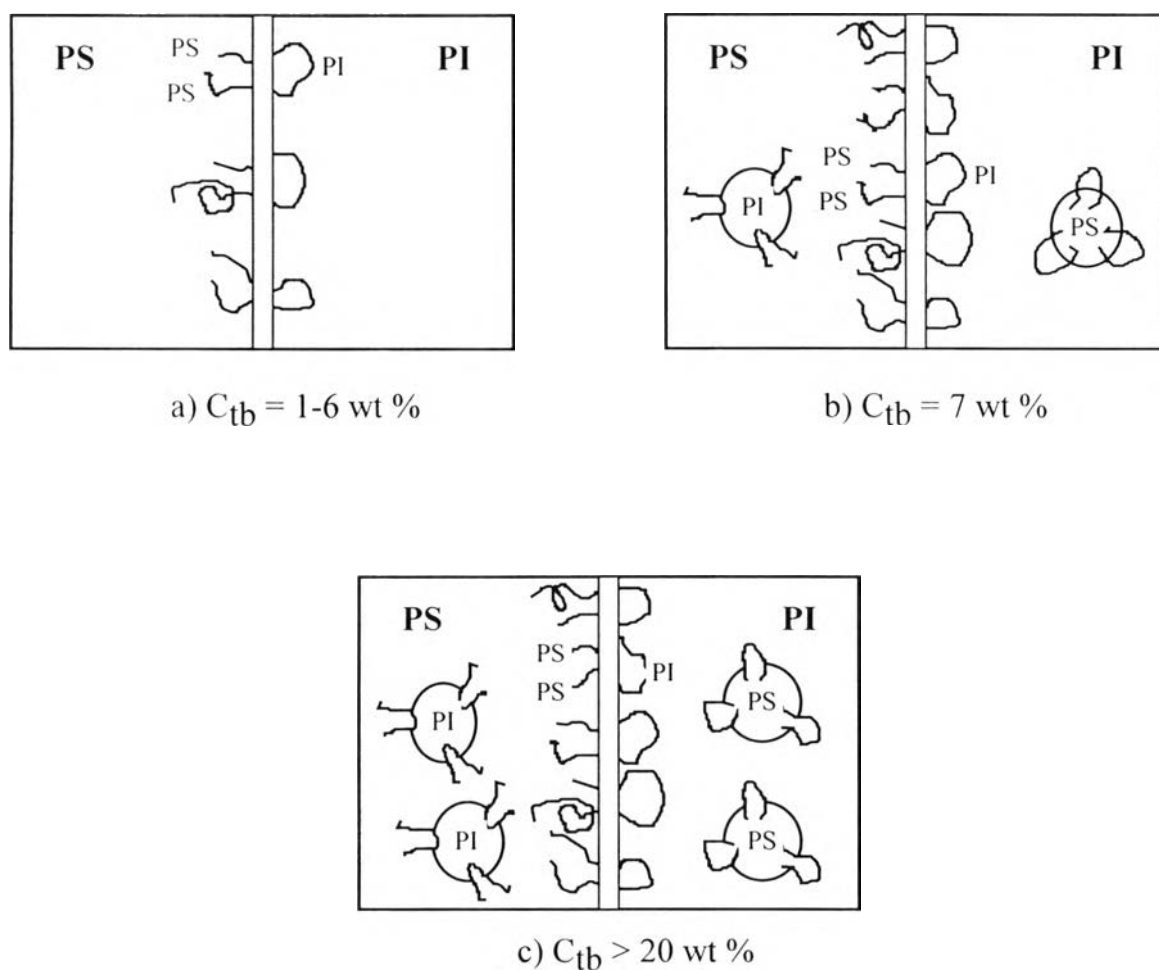
## CHAPTER IV

### DISCUSSION

#### 4.1 Model of Micelle Formation

Studying of thermal and mechanical properties is the one way to look at the compatibility of polymer blends. Normally, a stable polymer blends might be produced from immiscible polymers by using “compatibilizers.” Just as a surfactant can stabilize oil-water mixtures, it should be possible to enhance the stability and properties of an immiscible polymer blend by adding a “compatibilizing” polymer, usually a block or graft copolymer. The measurement of storage and loss moduli as function of temperature is one of various methods for determining the thermal properties of polymer blends. A miscible one-phase blends should have only one  $T_g$ , whereas a immiscible two-phase blends should have two glass transitions that closely approximate those of the individual polymers.

Both thermal and mechanical properties of the PS/PI blends can be described by the model in **Figure 4.1**. Addition of a small amount of block copolymer decreases the size of the dispersed PS phase (Figure 3.12b), consistent with emulsification effect.



**Figure 4.1** Ideal interfacial morphology model of PS/PI-100 (40/60) blend as a function of the triblock copolymer contents.

From Figures 3.1 and 3.2, between 1-6 wt % of the triblock copolymer, there is no change in the alpha transition temperature because a small amount of the triblock copolymer content added influences only the interfacial adhesion between the two phases [Figure 4.1a]. Thus, the  $T_{\alpha}$ 's of the hard and soft phases remain unchanged. At 7 wt % of triblock copolymer which is the onset of micelle formation, micelles are formed in both the hard phase and the rubber phase [Figure 4.1b]. It should be noted that this is strictly speaking the limit of the compatibilising activity of the block copolymer. Above this

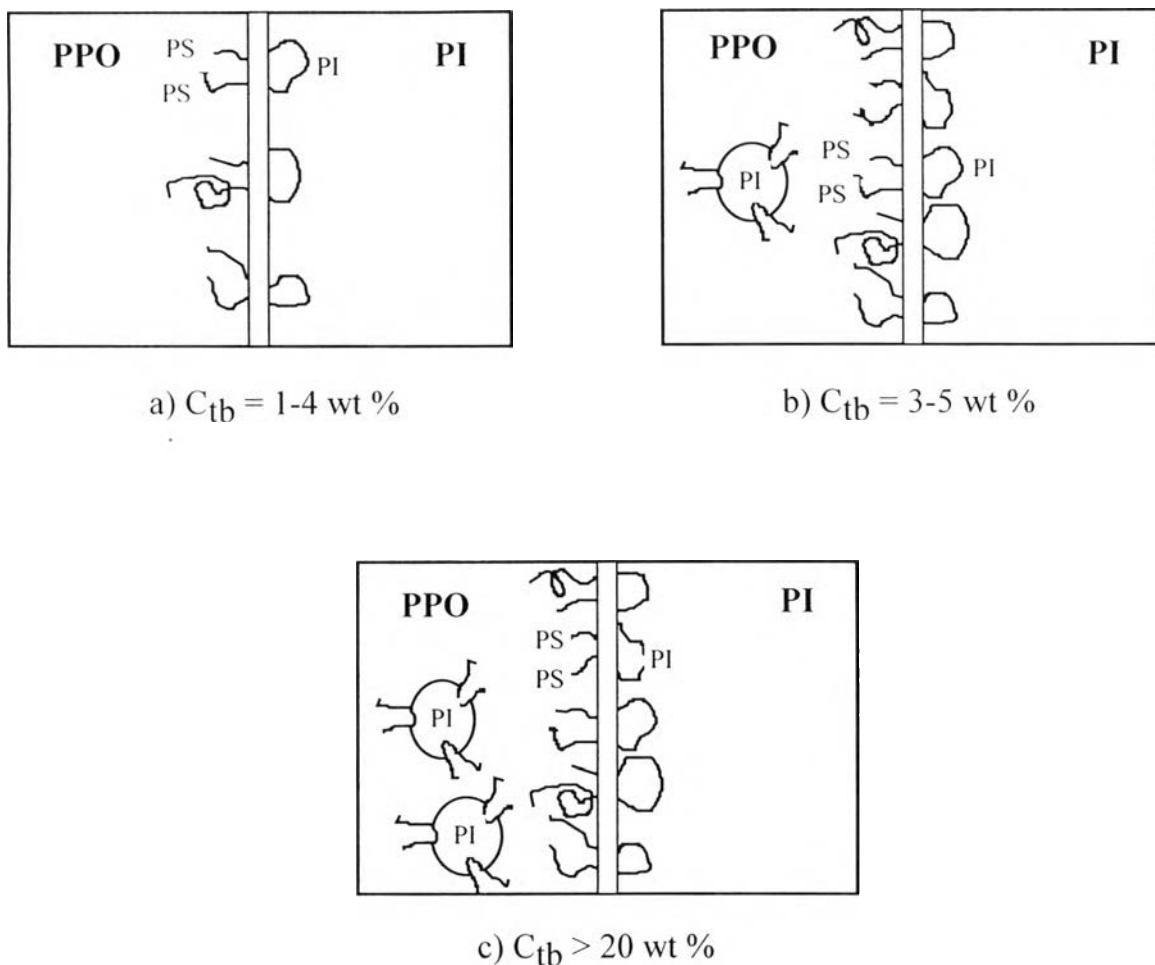
concentration, the structures formed by the block copolymer contribute to the materials properties. In the rubber phase, PS micelles occurs in the PI matrix and vice versa, therefore the hard phase exhibits two  $T_{\alpha}$  values, as shown in Figure 3.2. As noted earlier, the upper transition is believed to refer to  $T_{\alpha}$  of the amorphous PS homopolymer. The increase as the triblock copolymer is added may reflect enrichment in higher molecular weight of PS. The lower transition refer to the  $T_{\alpha}$  of PS micelles in the PI matrix. The decrease in this transition temperature as the triblock copolymer is added perhaps because of increase in coupling to the PI segments.

The mechanical properties of PS/PI-100 blends can be seen in Figure 3.5. At lower wt % of the triblock copolymer,  $G$  and  $\tau_y$  increase until reaching maximum at 7 wt % which is the onset of micelle formation in both PS and PI phases. The initial increase is evidence for effective compatibilization. Beyond that,  $G$  and  $\tau_y$  decrease until reaching a minimum value at 11 wt % presumably because the formation of triblock copolymer, micelles does not initially enhance mechanical strength. As the copolymer content increases further to 20 wt %,  $G$  and  $\tau_y$  increase again. This appears to correspond to the evolution of a network morphology (Figure 3.12d). Above 20 % copolymer,  $G$  and  $\tau_y$  decrease which presumably reflects the increase in the amount of soft phase in the material.

In these blends, the A segment (PS segment) of the block copolymer is identical to polymer A (PS homopolymer) and the B segment (PI mid-block) identical to polymer B (PI homopolymer). The working hypothesis is that segment A can penetrate polymer A and the segment B can penetrate polymer B in the neutral fashion since  $\chi = 0$ . The interfacial adhesion is improved as seen in the adherence of the matrix to the disperse phase in Figures 3.12b, c and d. Similar to the study by Reichert and Brown (1993) they found that a thin layer of a PS-PI diblock copolymer can increase the adhesion between PS

and crosslinked PI homopolymer. Doi et al. (1997) studied the strengthening polymer interfaces with a triblock copolymer. They found that the addition of PVP-b-dPS-b-PVP triblock copolymer to the interface between immiscible homopolymers PS and PVP can greatly enhance the fracture toughness of the interface. They also showed that the triblock copolymer form a “staple” structure at the interface with dPS block making a loop on the PS side of the interface and the PVP ends anchoring the “staple” in the PVP side. As in Doi’s report, our ideal interfacial morphology model shown in Figure 4.1 explores a similar configuration of triblock copolymer at the interface.

The other system that we mentioned is the mixing of the block copolymer with a chemically different homopolymer which forms miscible blends with a polymer made up of segments identical to those in one of the blocks of the copolymer. We refer specifically to the situation where this miscibility stems from an exothermic heat of mixing, that is, a favorable segment-segment interaction, which contrasts with the first case where mixing is athermal or entropic since the segments are identical with homopolymer. In our study, we studied the blends of the PPO/PI/P(S-b-I-b-S) system. Both thermal and mechanical properties of PPO/PI blends can be described by the model in **Figure 4.2**.



**Figure 4.2 Ideal interfacial morphology model of PPO/PI-100 (40/60) blends as a function of the triblock copolymer contents.**

At 3 wt % of triblock copolymer which is the onset of micelle formation, two hard-phase  $T_{\alpha}$  peaks are found (Figure 4.2b). Therefore,  $T_{\alpha}$  in Figure 3.4 splits into two lines. The upper transition is believed to refer to the amorphous PPO homopolymer, the small increase with added copolymer may be due to enrichment in higher molecular weight species. The lower transition refer to the PPO homopolymer in the vicinity of PS segments of the PI micelles and PS segments at the interface and possibly at higher copolymer content due to PS micelles in the PI phase. The decrease is due to the progressive increase in

exothermic interaction between PS-PPO. Previous work of Tucker and Barlow (1988) found that PPO and PS are miscible at all compositions, hence  $T_{\alpha}$  of the PPO homopolymer and PS segment blends has a single  $T_{\alpha}$  between PPO and PS. In this study,  $T_{\alpha}$ 's of the hard phase shifts due to this reason.

Schultz and Beach (1977) have examined the glass transition behavior of blends of PPO with a poly(styrene-*b*-butadiene-*b*-styrene) copolymer (SBS). From the rubber phase  $T_g$ , they found a single, composition-dependent  $T_g$  corresponding to PPO-PS mixtures, suggesting that the PPO is completely incorporated into the PS domains.

The same model can be used to describe the mechanical properties of PPO/PI-100 blends of Figure 3.6. At 1-4 wt % of the triblock copolymer,  $G$  and  $\tau_y$  increase monotonically, suggesting an evidence for effective compatibilization (Figure 4.2a). This is accompanied by a decrease in size of the dispersed PPO phase domains (emulsification, Figure 3.13b). At 5 wt % of the triblock copolymer,  $G$  and  $\tau_y$  show no significant change at the onset of micelle formation in the PPO phase as indicated in the appearance of a new hard phase  $T_{\alpha}$  transition. The values of  $G$  and  $\tau_y$  continue to increase smoothly up to 20 wt % of triblock copolymer. As for the PS/PI-100 system, this appears to reflect evolution of a network morphology (Figures 3.13c and d). For the shear yield strain, at 1-7 wt % of triblock copolymer,  $\gamma_y$  is independent of triblock copolymer content. Beyond 9 wt % of triblock copolymer,  $\gamma_y$  decreases monotonously due to the increase in volume of the PI phase which produces more ductile behavior.

## 4.2 Stress Relaxation and Relaxation Spectrum

Stress relaxation and relaxation spectrum are interesting properties which reveal the intrinsic nature of energy dissipation in polymer blends. The stress relaxation functions of the PS/PI-100 blends show a power law behavior,  $G(t) \approx t^{-n}$  as seen in Figure 3.8. The power-law relaxation is presumably dominated by the more molecule PI component. Consistent with the power-law decay, the relaxation spectrum is essentially rectangular (white noise). As expected  $G_g$  increases with the addition of the triblock copolymer following the increase in  $G$  and  $\tau_y$

For PPO/PI-100 blends, the shape of the stress relaxation is quite different from PS/PI-100 blends and appears to be close to an exponential decay. The reason for this is not clear, but may reflect the strong interaction between PS segment of the copolymer and PPO homopolymer. The relaxation spectrum, a single narrow (exponential) peak is seen in Figure 3.11a. At higher wt % of triblock copolymer content, this peak moves to the left, i.e. to small relaxation. The presence of the copolymer enhances the stress relaxation rate, for reasons which are unclear at present.

For relaxation phenomena, Aklonis (1987) defined a steepness index (SI) as the maximum of the negative slope of a stress relaxation curve in the glass transition region. They found that while polyisobutylene has a SI of about 0.5, PMMA has a value of about 1.0 and PS is close to 1.5. Aklonis treated the data theoretically, using the Rouse-Boeche-Zimm bead and spring model, based in turn on the Debye damped torsional oscillator model. Aklonis concluded that SI values equal to 0.5 represented a predominance of intramolecular force and a SI of 1.5 represented a predominance of intermolecular forces. A SI of 1.0 was an intermediate case. This is in agreement with the stress relaxation results shown in Figure 3.10 for the higher wt % of triblock copolymer, the stress

relaxation shows steeper slope. The strong favorable interaction between PS segments and PPO homopolymers, as indicated by Ziaee and Pual (1996), exists because of a specific interaction between  $\pi$  hydrogen bond and  $\pi$ -orbital in PS aromatic ring and methyl groups in PPO.

### 4.3 Morphology

Microscopy is a useful tool to determine if a blend is single or multiphase. The SEM has been used to investigate adhesion between EVA particles and PBT matrix (Pilali and Pezzin, 1984). Jo et al. (1996) also used SEM to study the effect of the molecular structure of the styrene-isoprene-styrene block copolymer on interfacial tension, the morphology and the interfacial adhesion of PS/PI blends.

Generally, the major component constitutes the continuous phase and the minor component forms discrete domains, with the block copolymer located at the interface as an emulsifier, its block segment selectively localized in each homopolymer (Adedeji et al., 1996). In our PS/PI blends, we observed that the PS forms the dispersed phase in a PI matrix seen in Figure 3.12a. On addition of the triblock copolymer, the particle size of dispersed PS domain decreases (emulsification) and it appears that interfacial adhesion is enhanced since the triblock copolymer can reside at the interface and anchor between PS and PI phases. This is evident in that some of the PS dispersed phase domains appear to fracture, and there is adherence of matrix to the PS domains. Jo et al. (1996) studied the fracture surface of PS/PI (75/25) blends with addition of 1 wt % of P(S-b-I) diblock copolymer. They found that the domain size of dispersed phase is reduced when the block copolymer is added. These results are consistent with the thermal and mechanical properties. At the level of the



triblock copolymer increased up to 20 wt %, there is evolution to a fibrillar structure for the PI major phase.

The morphology of PPO/PI-100 blends can be seen in Figure 3.13. The SEM photographs show clearly the decrease in size of the PPO dispersed domains with the addition of the triblock copolymer. This is consistent with our data from thermal and mechanical properties. As triblock copolymer content is increased up to 20 wt %, there is again a gradual evolution to a network fibrillar morphology.