

CHAPTER III

RESULTS

3.1 Alpha Transition Temperature

It is well known that amorphous polymers can exhibit two distinctly different types of mechanical behavior. Some polymers, are hard, rigid, glassy plastics at room temperature, while others, are soft, flexible rubbery materials. There is some temperature, or a narrow range of temperatures, below which an amorphous polymer is in a glassy state, and above which it is rubbery. This temperature is known as the *glass transition temperature*, T_g (Rosen, 1993).

The glass transition temperature T_g of a polymer is the temperature at which the molecular chains attain sufficient energy to overcome attractive forces and can move vibrationally, and translationally. The number and locations of the T_g 's provide much insight into the nature of a polymer blends. For example, a miscible one-phase blend should have only one T_g , whereas a two-phase blend should have two glass transitions, one for each phase.

The measurement of transition temperature can assist in the determination of compatibility of amorphous polymer blends (Folkes and Hope, 1993). For immiscible two-phase systems, two T_g 's that closely approximate those of the individual polymers are expected. The addition of triblock copolymer will improve the adhesion between the two polymer phases, which is critical for stress transfer between these phases. In addition, it will lower the interfacial tension between phase and contribute to their stability against gross phase separation during processing. If a blend becomes more

compatible, the transition temperature of each phase would shift closer together.

The transition temperature is usually obtained from a plot of G' and G'' versus temperature. The maxima in loss modulus (G'') is used as the definition of the alpha transition temperature (T_{α}). For the α -transition the portion of molecule excited may be from 10 to 50 atoms or more (Brandruys and Immergut, 1975). Alpha transition temperature (T_{α}) can be associated with the glass transition temperature (T_g). T_g indicates the change in the heat capacity which reflects a fundamental change in molecular motion (Sperling, 1993).

T_g can be considered the most important material characteristic of a polymer as far as mechanical properties are concerned. In view of the great practicable importance of the glass transition temperature, a table of T_g values for many common polymers is given in **Appendix II**.

3.1.1 Effect of Triblock Copolymer Content on The Alpha Transition Temperature of PS/PI-100 Blends

To study the effect of the triblock copolymer concentration on the alpha transition temperature, the composition for the PS/PI-100 blends was fixed at 40/60 and the triblock copolymer concentration was varied from 1-20 wt %. PS/P(S-b-I-b-S)/PI-100 blends are composed of a rubber phase and a hard phase, where the rubber phase is PI-100 homopolymer and PI segments, the hard phase is PS homopolymer and PS segments.

Figure 3.1 shows the loss modulus at frequency of 1 rad/second of hard phase of PS/PI-100 (40/60) blends as a function of temperature and triblock copolymer content. There are no changes in the alpha transition temperature with the addition of the triblock copolymer between 1-5 wt %. But at 7 wt % or more, the alpha transition temperature shifts to a lower temperature and a higher temperature where we can identify two peaks.

Figure 3.2 summarizes the effect of triblock copolymer content on the alpha transition temperature of the hard phase of PS/PI-100 (40/60) blends. From 1-5 wt % of the triblock copolymer, there is little or no change in the alpha transition temperature. At 7 wt % of the triblock copolymer, a new hard-phase T_{α} peak appear. Although we cannot be certain, it appears likely that the upper transition refer to T_{α} of the amorphous PS and the lower transition refers to T_{α} of PS micelles in the PI matrix. The lower T_{α} is believed to arise because there PS segments are attached covalently to liquid-like PI segments and further are the higher energy stage in the micellar phase.

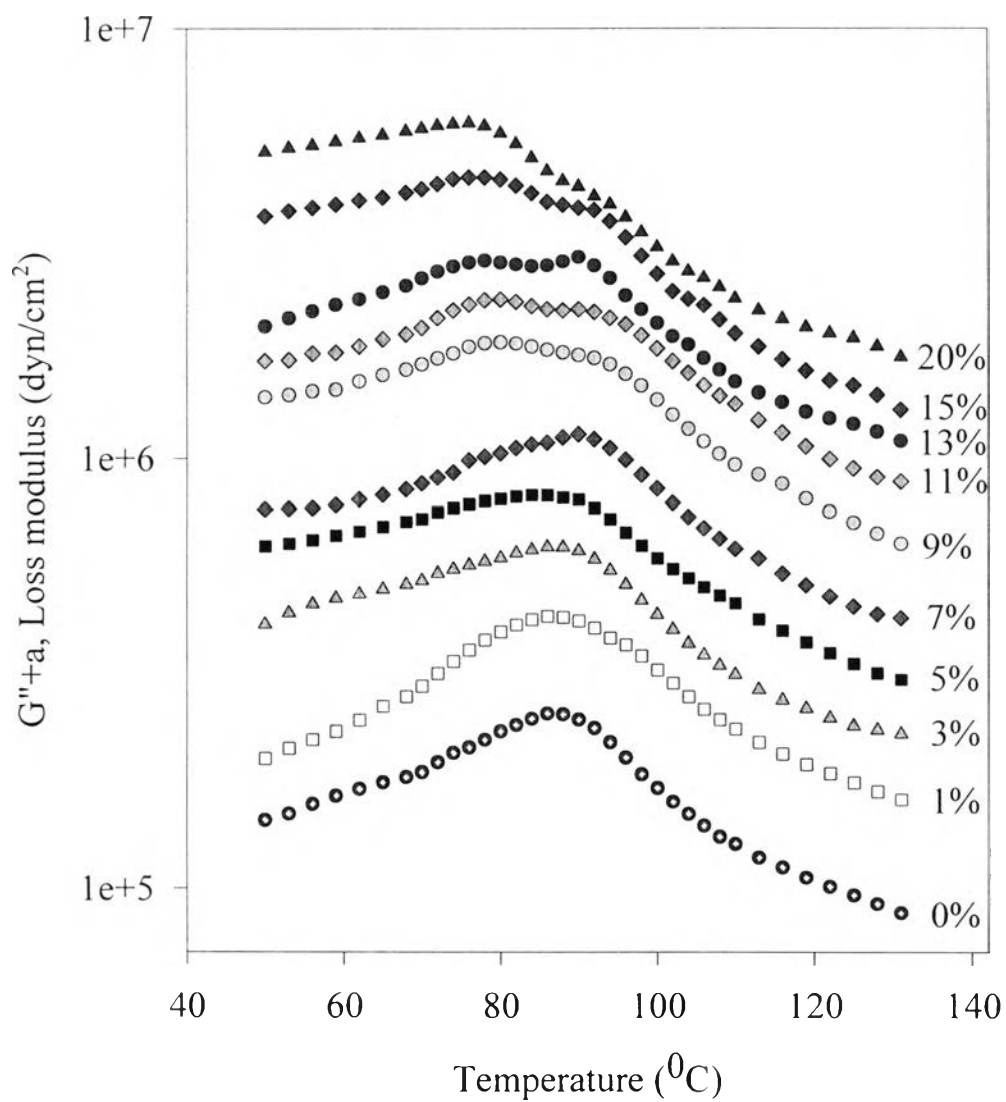


Figure 3.1 Loss modulus at frequency of 1 rad/second of hard phase of PS/PI-100 (40/60) blends as a function of temperature and the triblock copolymer contents. Each curve is offset vertically by an amount of 0-20 wt % of triblock copolymer.

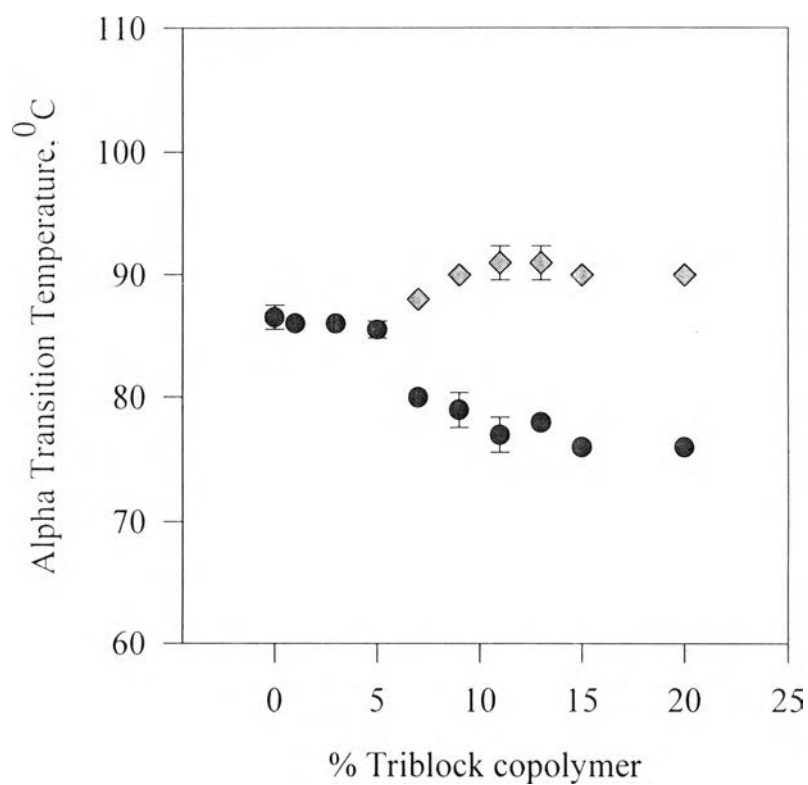


Figure 3.2 Effect of the triblock copolymer content on the alpha transition temperature of the hard phase of PS/PI-100 (40/60) blends.

Table 3.1 Effect of the triblock copolymer contents on the alpha transition temperature of PS/PI-100 (40/60) blends

% Triblock copolymer	T_{α} of rubber phase ($^{\circ}\text{C}$)	T_{α} of hard phase ($^{\circ}\text{C}$)	ΔT_{α}	% change in T_{α}
0%	-60	87	147	0
20%	-57	76	133	9

Table 3.1 lists the alpha transition temperatures for the hard and soft phases and the difference between the two alpha transition temperatures (ΔT_{α}). We see that ΔT_{α} decreases only slightly by 9 % with an addition of 20 wt % of triblock copolymer. This is expected because PS and PI are highly immiscible.

3.1.2 Effect of Triblock Copolymer Content on The Alpha Transition Temperature of PPO/PI-100 Blends

The effect of triblock copolymer content on the alpha transition temperature of PPO/PI-100 blends was studied for the composition ratio of 40/60 and triblock copolymer concentration was varied between 1-20 wt %. PPO/P(S-b-I-b-S)/PI-100 blends are composed of a rubber phase and a hard phase, where the rubber phase is PI-100 homopolymer and PI segments, the hard phase is PPO homopolymer and PS segments.

Figure 3.3 shows loss modulus at frequency of 1 rad/second of the hard phase of PPO/PI-100 (40/60) blends as a function of temperature and triblock copolymer contents. We can see that the T_{α} is about 180°C for the PPO phase shifts only slightly toward a lower temperature as more the triblock copolymer is added. At 3 wt % or more triblock copolymer, a second peak at around 80-100°C can be identified, presumably due to formation of P(S-b-I-b-S) micelles.

Figure 3.4 shows the effect of triblock copolymer content on the T_{α} of the hard phase of PPO/PI-100 (40/60) blends. We can see that the hard phase T_{α} region splits into two transitions with the addition of 3 wt % of the triblock copolymer. Again, it is not certain what are the identical origins of these peaks, but it is believed that the upper transition refers to amorphous PPO homopolymer and the lower transition, which increases with added copolymer, reflects formation of block copolymer micelles and comes from

the mixing of PPO homopolymer and PS segment at the interface between micelles and PPO.

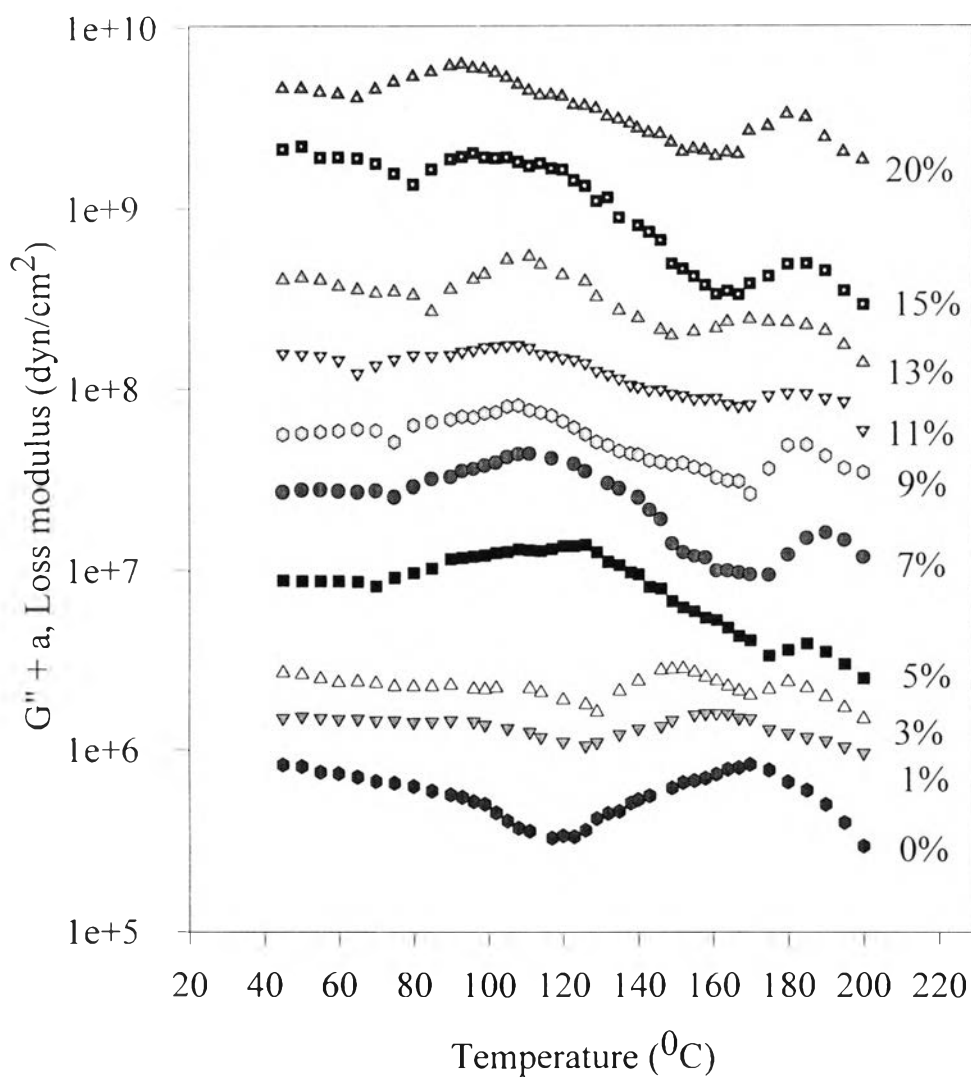


Figure 3.3 Loss modulus at frequency of 1 rad/second of hard phase of PPO/PI-100 (40/60) blends as a function of temperature and the triblock copolymer contents. Each curve is vertically shifted by an amount of 0-20 wt % of triblock copolymer.

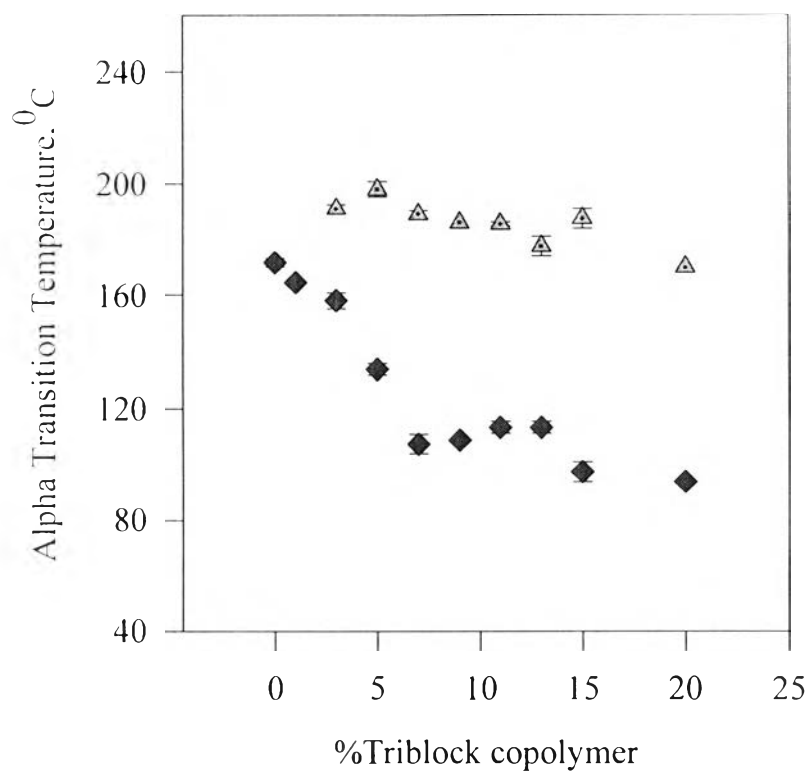


Figure 3.4 Effect of triblock copolymer contents on the alpha transition temperature of the hard phase of PPO/PI-100 (40/60) blends.

Table 3.2 Effect of the triblock copolymer contents on the alpha transition temperature of PPO/PI-100 (40/60) blends

% Triblock copolymer	T_{α} of rubber phase ($^{\circ}\text{C}$)	T_{α} of hard phase ($^{\circ}\text{C}$)	ΔT_{α}	% change in T_{α}
0%	-61	172	233	0
20%	-50	94	144	38

Table 3.2 shows the alpha transition temperature values of each phase together with the difference between the two alpha transition temperatures (ΔT_{α}). We can see that T_{α} of each phase shifts closer together when 20 wt % of the triblock copolymer is added. ΔT_{α} changes by 38 % because of the effect of exothermic interaction.

3.2 Mechanical Properties

In this study, mechanical properties studied were the shear modulus (G), the shear yield stress (τ_y) and the shear yield strain (γ_y) which were examined by using a rheometer in step rate testing mode. Shear modulus was obtained from the initial slope of stress-strain curve. It can be used to infer adhesion between phases. Shear yield stress and shear yield strain were obtained from the initial stress-strain curve with a line offset of 0.2 % from the origin.

3.2.1 Effect of Triblock Copolymer Content on The Mechanical Properties of PS/PI-100 Blends

To study the effect of the triblock copolymer concentration on the mechanical properties, the composition for the PS/PI-100 blends was fixed at 40/60 and triblock copolymer concentration was varied between 1-55 wt %.

Figure 3.5 shows the effect of the triblock copolymer content on mechanical properties of PS/PI-100 (40/60) blends at 25°C. At this temperature, the PS phase is in the glassy state and the PI phase is in the rubbery state. We can see that G and τ_y increase monotonically with additions of triblock copolymer until reaching a maximum value at 7 wt % of the triblock copolymer. At this concentration from Figures 3.1 and 3.2 we know that micelle formation occurs. Beyond that, G and τ_y exhibit a small bud

significant decrease until reaching a minimum value at 11 wt % and then increase again as more triblock copolymer is added. At around 20 % added copolymer, a substantial decrease in G and τ_y occurs and G and τ_y remain at lower value as further amount of the triblock copolymer is added. For the shear yield strain, we see that there appears to be a same maximum at the concentration of the triblock copolymer of 7 wt % corresponding to the onset micelle formation which is consistent with the decrease in G . At higher wt % of the triblock copolymer, ϵ_y appears independent of triblock copolymer content. within experimental uncertainty.

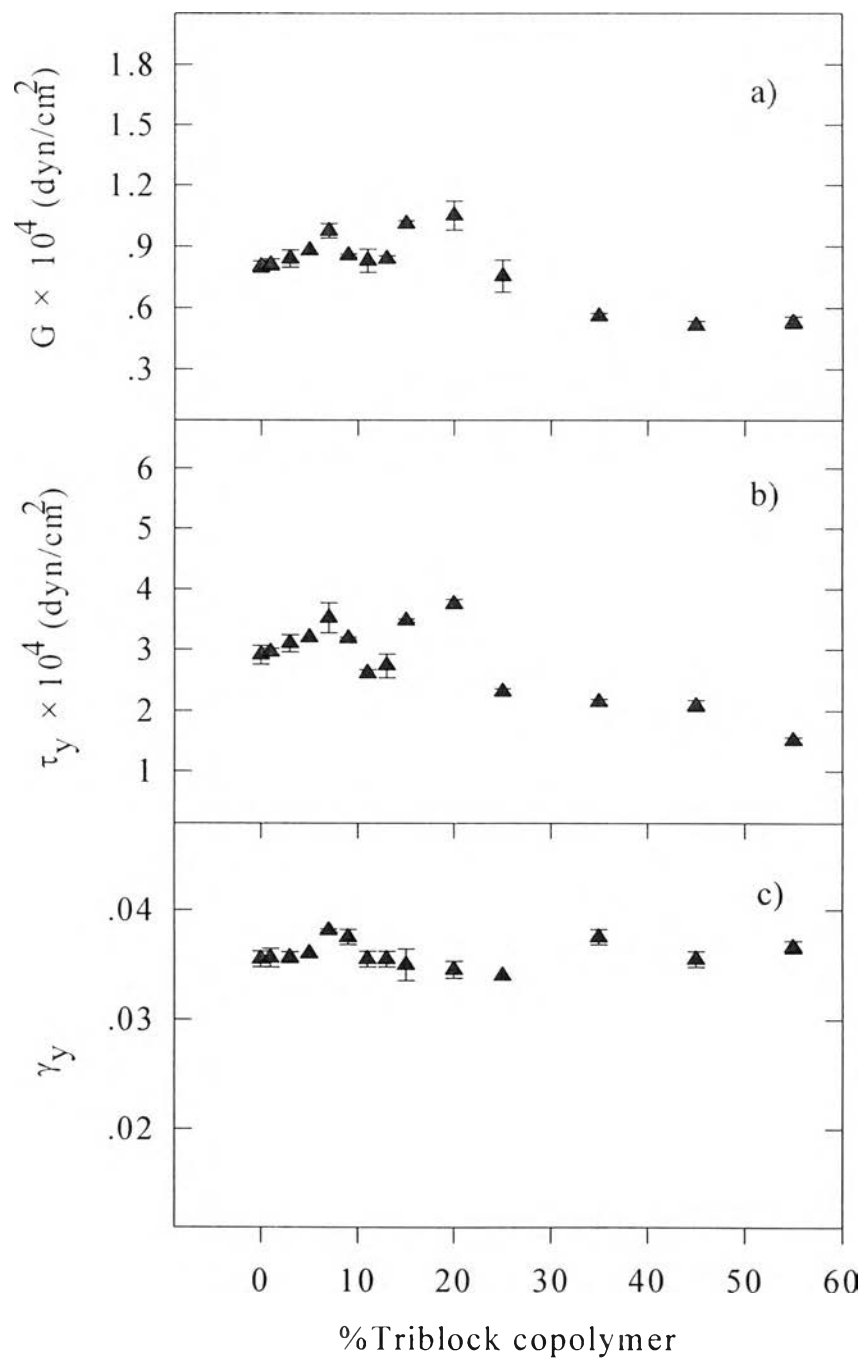


Figure 3.5 Effect of triblock copolymer content on the mechanical properties of PS/PI-100 (40/60) blends at 25°C: a) shear modulus; b) shear yield stress; c) shear yield strain.

3.2.2 Effect of Triblock Copolymer Content on The Mechanical Properties of PPO/PI-100 Blends

To study the effect of the triblock copolymer concentration on the mechanical properties, the composition for the PPO/PI-100 blends was fixed at 40/60 and triblock copolymer concentration was varied between 1-55 wt %.

Figure 3.6 depicts the effect of the triblock copolymer content on mechanical properties of PPO/PI-100 (40/60) blends at 25°C. At this temperature, the PPO phase is in the glassy state and the PI phase is in the rubbery state. It can be seen that G and τ_y increase monotonically with addition of triblock copolymer until reaching a maximum value at 20 wt % of the triblock copolymer. There is little discernible change in G and τ_y at the concentration of 5 wt % of triblock copolymer where the onset of micelle formation in PPO phase occurs based on Figures 3.3 and 3.4. Beyond 20 wt %, G and τ_y decrease monotonically as further amount of the triblock copolymer is added. For the shear yield strain (Figure 3.6c), we can see that γ_y is nearly constant with the initial addition of the triblock copolymer. Beyond 9 wt % of the triblock copolymer the shear yield strain decreases monotonically as more triblock copolymer is added. The results in Figures 3.5 and 3.6 indicate that the change in mechanical properties at the onset of micellisation in both PS/PI-100 and PPO/PI-100 blends is relatively small. In each blend there are pronounced in mechanical properties decrease when adding block copolymer above 20 wt %. In order to understand these changes in mechanical properties, it is necessary to attempt to characterize the molecular structure or morphology of the blends

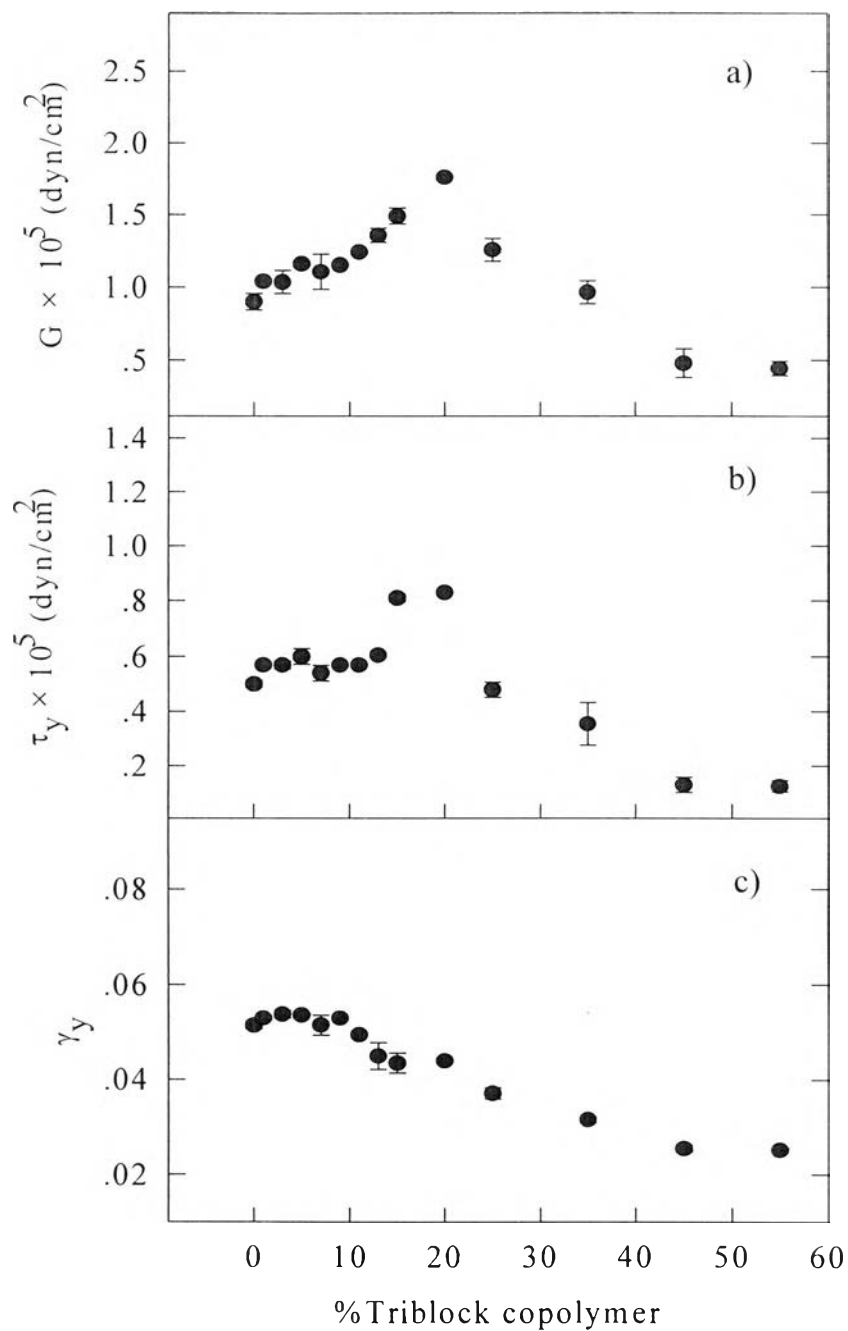


Figure 3.6 Effect of the triblock copolymer content on the mechanical properties of PPO/PI-100 (40/60) blends at 25°C: a) shear modulus b) shear yield stress; c) shear yield strain.

3.3 Stress Relaxation and Relaxation Spectrum

The stress relaxation phenomenon is viewed as the most fundamental manifestation of viscoelasticity of polymers. A stress relaxation test involves a rapid, preselected deformation of the material followed by a measurement of the stress required to maintain the strain over time.

A stress relaxation modulus $G(t)$ that decreases with time can then be calculated by dividing the stress, measured as a function of time, by the constant strain.

Before discussing the stress relaxation and relaxation spectrum results on PS/PI-100 and PPO/PI-100 blends, the characteristics of $G(t)$ for melts of nearly monodisperse linear polymers, illustrating the glassy, transition, plateau, and terminal zones of response, are described in **Figure 3.7** (Mark et al. 1993).

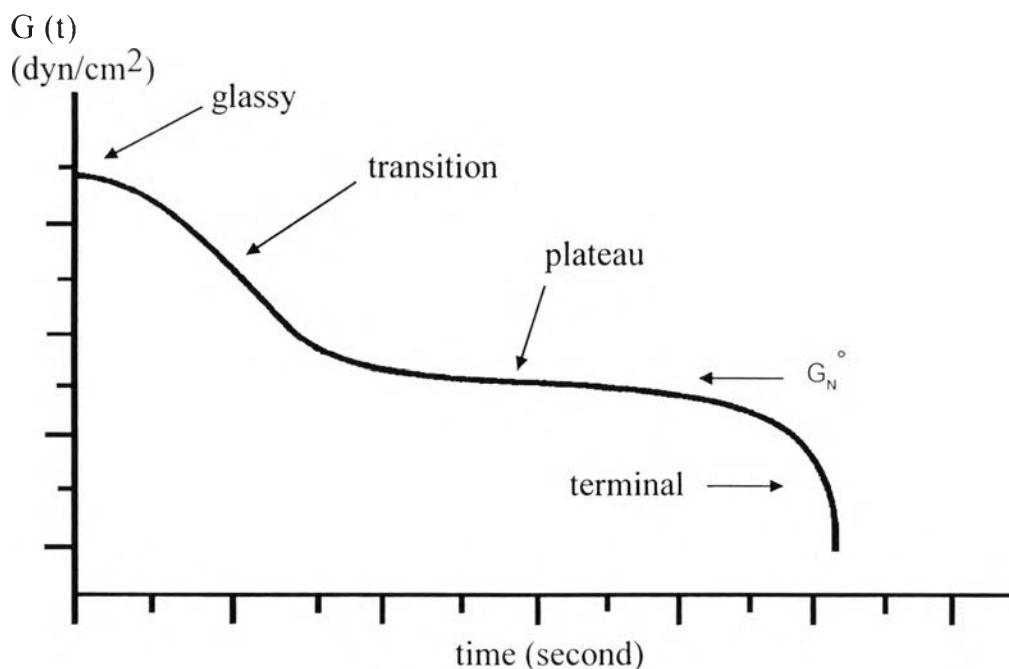


Figure 3.7 Shear stress relaxation function for a typical polymer melt.

At very short times, the response is glassy. The modulus for glass response, G_g is large and essentially constant. The modulus begins to decrease in the same range of times that the chains begin to relax locally, and it continues to decrease as the relaxation propagates over progressively longer chain distances. For short chains, the relaxation simply proceeds smoothly and monotonically to zero. For long chains, however, the initial relaxation rate, slow perceptibly, and the modulus remains relatively constant over some range of times before resuming a more rapid relaxation rate to full equilibrium.

This intermediate zone, or plateau, separates the short-time relaxation region, called the transition zone, where the large-scale chain has little effect, and the long time-relaxation region, called the terminal zone. Response in the plateau zone resembles that of a rubber network and arises from the fact that in this time scale the entanglements between chains delay stress relaxation. The width of the plateau zone increases rapidly with chain length, but the plateau modulus, G_N° is independent of chain length.

3.3.1 Effect of Triblock Copolymer Content on Stress Relaxation and Relaxation Spectrum of PS/PI-100 Blends

To study the effect of the triblock copolymer concentration on the stress relaxation and relaxation spectrum, the composition for the PS/PI-100 blends was fixed at 40/60 and triblock copolymer concentration was varied between 1-20 wt %.

The stress relaxation moduli ($G(t)$) of PS/PI-100 blends without triblock copolymer, with 1 wt % of triblock copolymer, with 9 wt % of triblock copolymer and with 20 wt % of triblock copolymer are shown in Figure 3.8. As expected the instantaneous glassy modulus, G_g increases with the addition of triblock copolymer. For each material, $G(t)$ shows a initially slow power law relaxation, $G(t) \approx t^{-n}$ with $n \approx 0.166$ (Figure 3.8a-d), followed

by the sharp decrease. The addition of block copolymer does not appear to have a significant effect on the slow stress relaxation process.

Figure 3.9 shows the effect of the triblock copolymer on the relaxation spectrum of PS/PI-100 blends. The results show a broad band “white-noise” spectrum which appears essentially unaffected by triblock copolymer content. The two apparent minimum peaks are viewed as spurious noise peak since there is no corresponding visible features in $G(t)$.

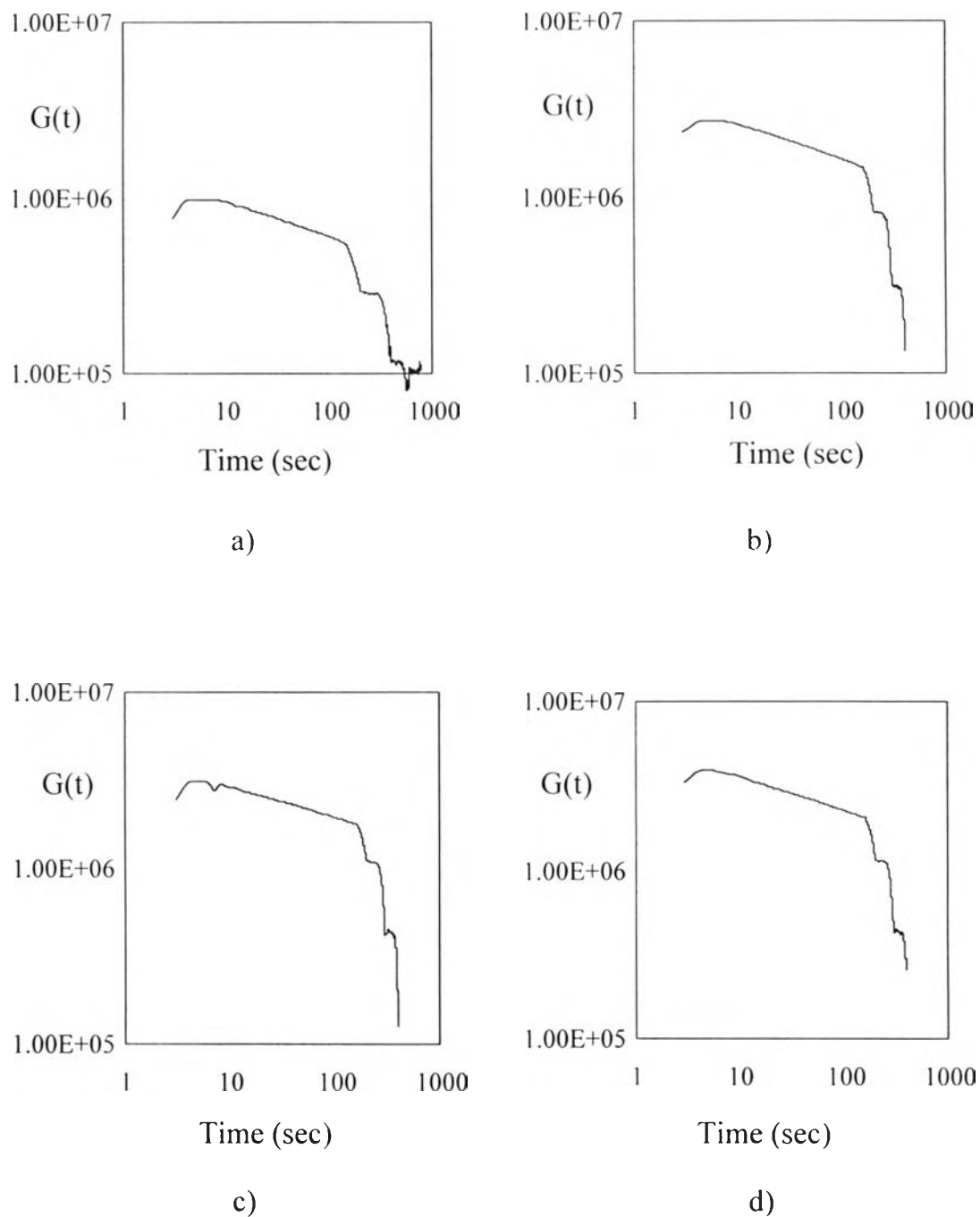


Figure 3.8 Effect of the triblock copolymer content on stress relaxation ($G(t)$) of PS/PI-100 (40/60) blends at 50°C : a) 0 wt %; b) 1 wt %; c) 9 wt %; d) 20 wt %.

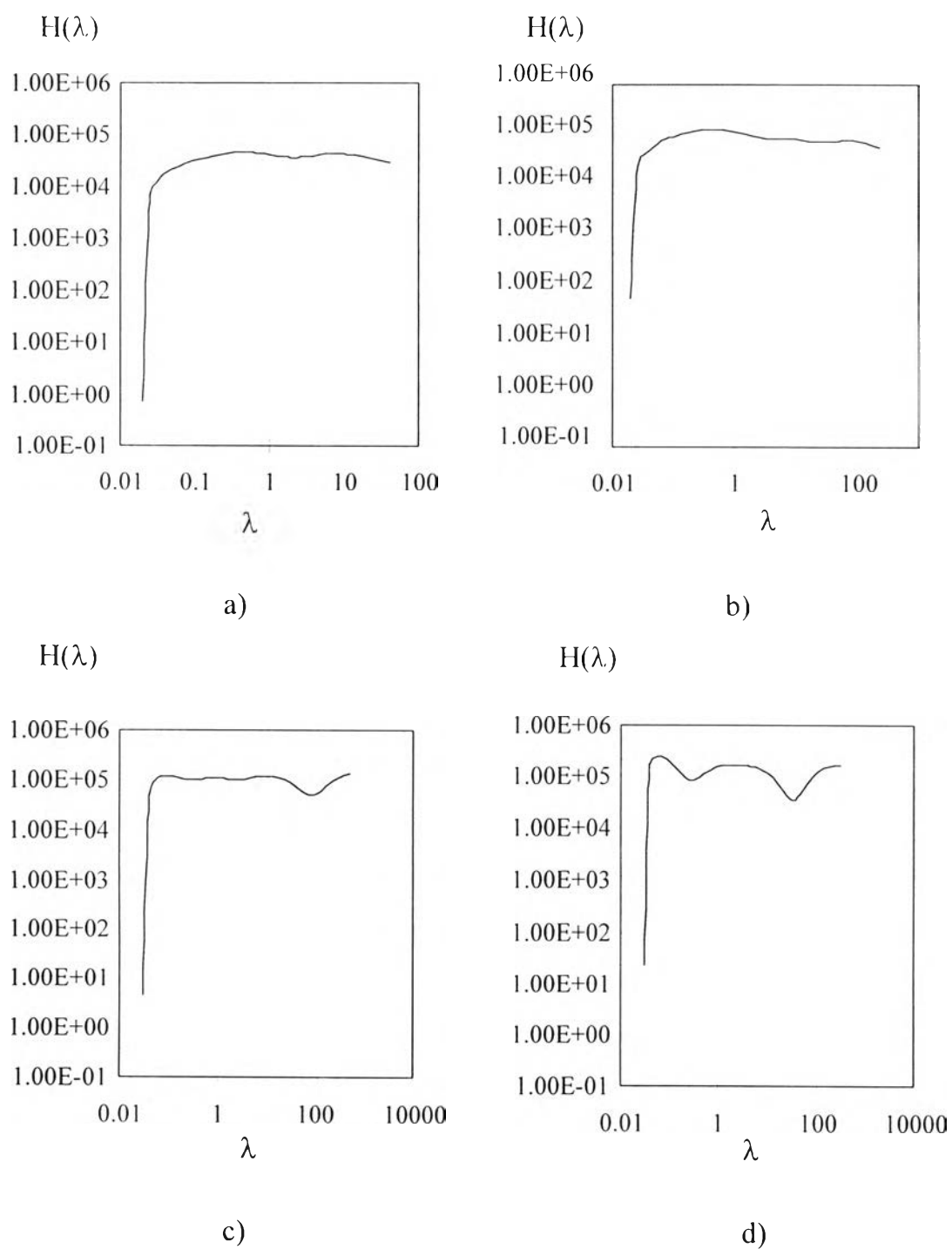


Figure 3.9 Effect of the triblock copolymer content on relaxation spectrum ($H(\lambda)$) of PS/PI-100 (40/60) blends at 50°C : a) 0 wt %; b) 1 wt %; c) 9 wt %; d) 20 wt %.

3.3.2 Effect of Triblock Copolymer Content on Stress Relaxation and Relaxation Spectrum of PPO/PI-100 blends

To study the effect of triblock copolymer concentration on the stress relaxation and relaxation spectrum, the composition for the PPO/PI-100 blends was fixed at 40/60 and triblock copolymer concentration was varied between 1-20 wt %.

Figure 3.10 shows the stress relaxation function of PPO/PI blends as a function of wt % of triblock copolymer. It can again be seen that the instantaneous glassy modulus G_g increases with increasing amount of triblock copolymer. It is also apparent that there is a rapid initial decay of stress, followed by a slower process. This is a quite different form of stress relaxation to that of the PS/PI-100 blends. Also, the rate of the initial decay increases as more amount of the triblock copolymer is added (Figure 3.10a-d).

Figure 3.11 shows the relaxation spectrum of the PPO/PI blends with and without the triblock copolymer. The shape of the relaxation spectrum is quite different from that of the PS/PI-100 blends, showing a narrow exponential as triblock copolymer content increases.

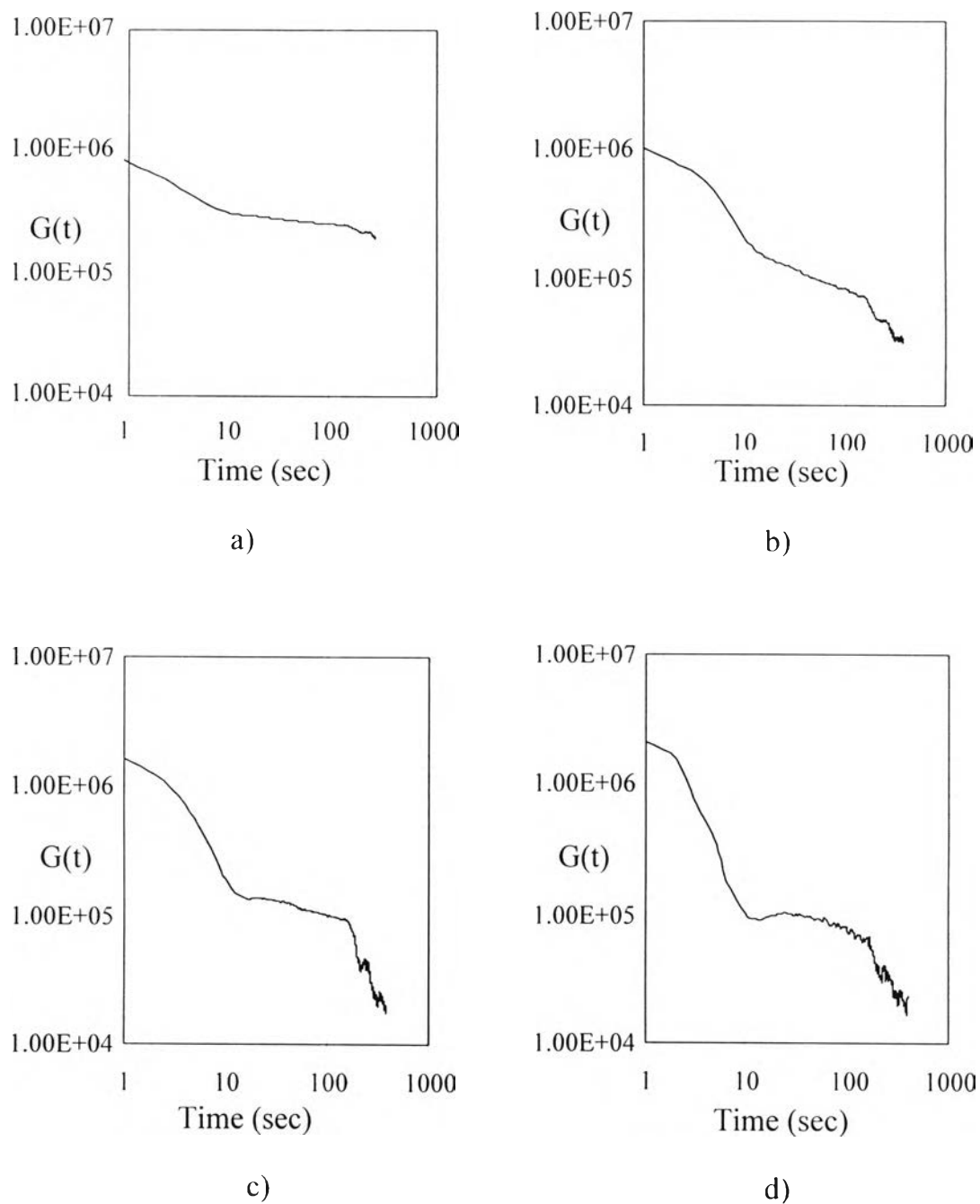


Figure 3.10 Effect of the triblock copolymer content on stress relaxation ($G(t)$) of PPO/PI-100 (40/60) blends at 50°C : a) 0 wt % ; b) 1 wt % ; c) 9 wt % ; d) 20 wt %.

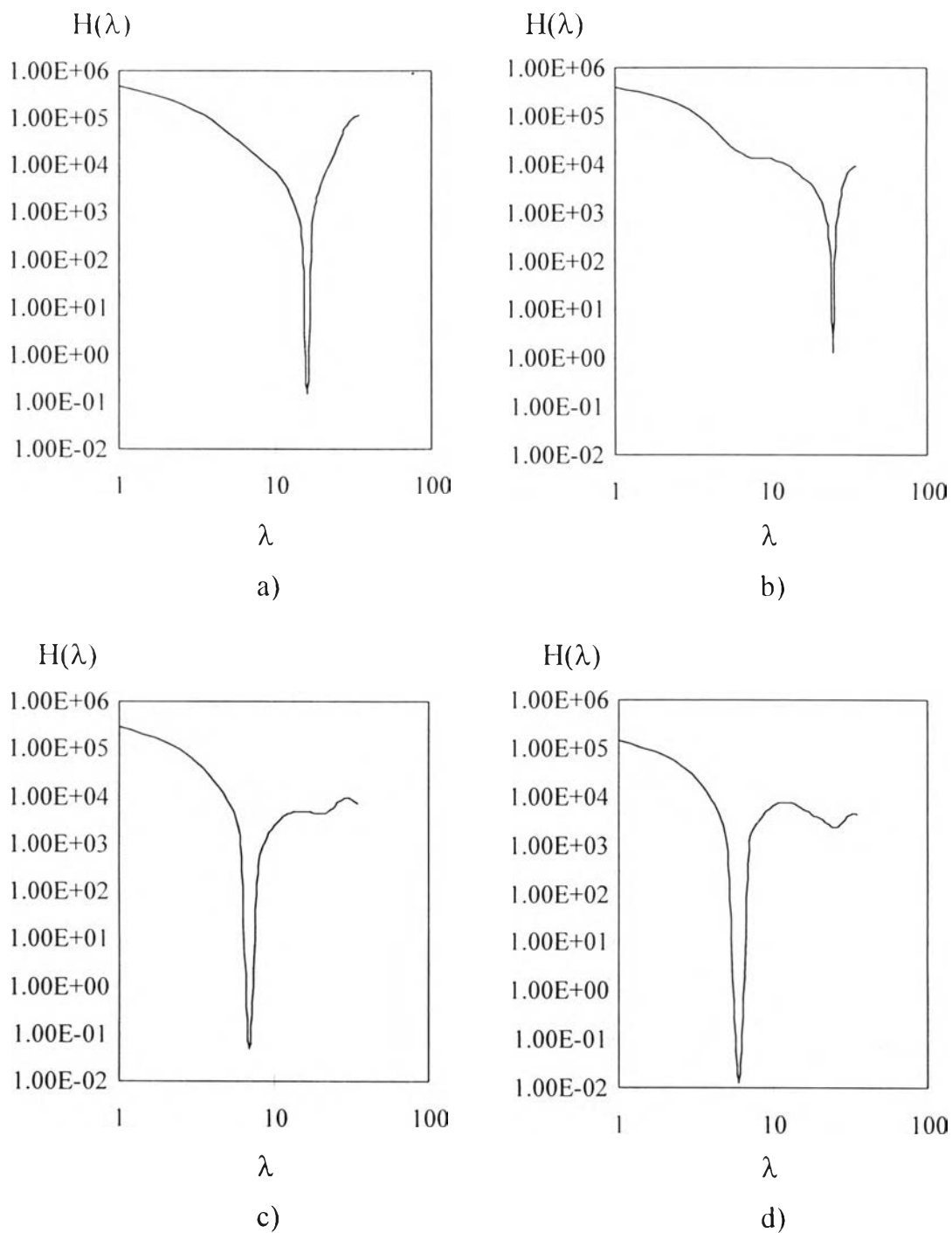


Figure 3.11 Effect of the triblock copolymer content on relaxation spectrum ($H(\tau)$) of PPO/PI-100 (40/60) blends at 50°C : a) 0 wt % ; b) 1 wt % ; c) 9 wt % ; d) 20 wt %.

3.4 Fracture Surface Morphology

To understand the molecular origin of the variation in mechanical properties, it is of interest to investigate the structure of the blends.

SEM is a popular method of observation the structure or morphology of polymer blends. The great advantages of this technique are the ease of measurement, range of readily accessible magnifications and depth of field.

3.4.1 Effect of Triblock Copolymer Content on Fracture Surface of PS/PI-100 Blends

To study the effect of the triblock copolymer concentration on the fracture surface morphology of PS/PI-100 blends, the composition for the PS/PI-100 blends was fixed at 40/60 and triblock copolymer concentrations were 0 wt %, 5 wt %, 9 wt %, and 20 wt %, respectively.

Each sample film was fractured in liquid nitrogen. In coating, the samples were mounted on stubs on the sputtering device and then coated with sputtered gold for 4 min. Coated samples were observed by SEM at an accelerating voltage of 5-25 kV and at a magnification of 1000.

Figure 3.12 shows the SEM micrographs of fracture surface of PS/PI-100 (40/60) blends, uncompatibilized and compatibilized with 5 wt %, 9 wt % and 20 wt % of the triblock copolymer, respectively. We can see that for the blend without triblock copolymer (Figure 3.12a), the fracture surface of the sample shows, clearly, the immiscibility and poor interfacial adhesion between PS dispersed phase and PI matrix. It can be seen in Figure 3.12a that the PS dispersed phase consists of elliptical particles with smooth surfaces. The major PI component of the blend forms the continuous matrix, while the minor PS component forms the dispersed phase (Vaidya et al., 1995). The size of the disperse phase decreases with addition of triblock copolymer (Figure 3.12b).

With the 5 wt % and 9 wt % of triblock copolymer (Figures 3.12b and c), the triblock copolymers reside at the interface between PS and PI phase and adhere to both phases. The increased interfacial strength is evident in that some of the dispersed phase particles are fractured and the continuous matrix is seen to adhere to mainly dispersed phase particles. With further increase of the triblock copolymer content to 20 wt % (Figure 3.12d), the morphology shows fibrillar structure for the PI major phase.

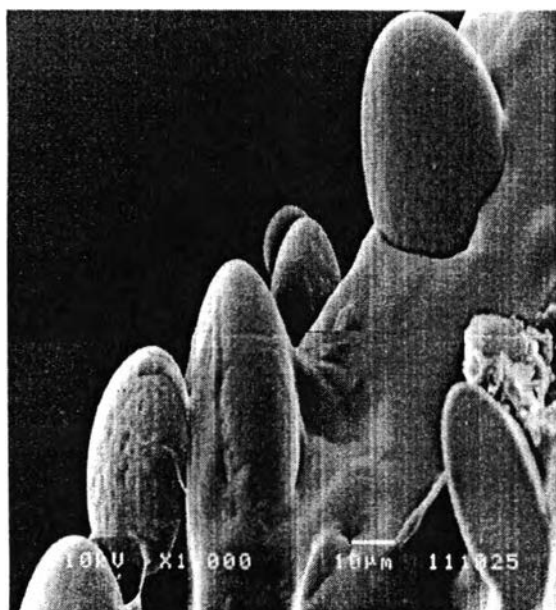
3.4.2 Effect of Triblock Copolymer Content on Fracture Surface of PPO/PI-100 Blends

To study the effect of triblock copolymer concentration on the fracture surface morphology of PPO/PI-100 blends, the composition for the PPO/PI-100 blends was fixed at 40/60 and triblock copolymer concentrations were 0 wt %, 3 wt %, 9 wt %, and 20 wt %, respectively.

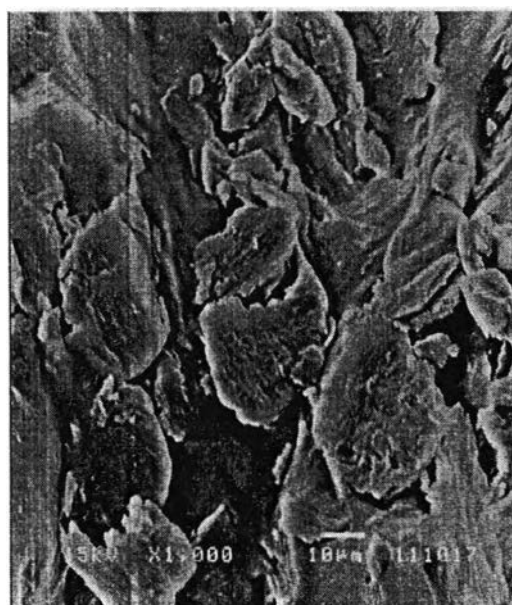
Each sample film was fractured in liquid nitrogen. In coating, the samples were mounted on stubs on the sputtering device and then coated with sputtered gold for 4 min. Coated samples were observed by SEM at an accelerating voltage of 5-25 kV and at a magnification of 1000.

SEM photographs in Figures 3.13a-d are the fracture surfaces of the PPO/PI-100 (40/60) blends uncompatibilized and compatibilized with 3 wt %, 9 wt %, and 20 wt %, respectively. Blending without triblock copolymer [Figure 3.13, a)], the particle shape of PPO dispersed phase is apparently elliptical. This is supported by the SEM micrographs in Figure 3.14 which shows the fracture surface of binary blend PPO/PI-100 (40/60) at various magnifications: a) x200, b) x500, c) x1000, and d) x2000, respectively. We can see that the particle shape of PPO dispersed phase is apparently elliptical at different magnifications.

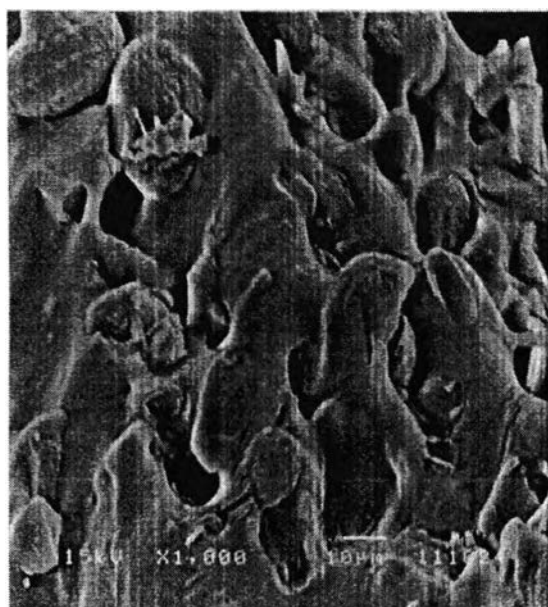
The addition of 3 wt % of the triblock copolymer to the interface between PPO and PI immiscible phase (Figure 3.13b), the size of the PPO dispersed phase becomes smaller (emulsification) and adherence of the matrix to the dispersed phase increases which would reflect an improvement in interfacial adhesion. At 9 wt % of triblock copolymer the morphology appears similar to a interpenetrating network, suggesting the block copolymer may produces a phase inversion (Adedeji et al., 1996). At 20 wt % of the triblock copolymer (Figure 3.13d), the triblock copolymer further promotes dispersion of the immiscible phases, as evidenced by the more uniform fracture surface.



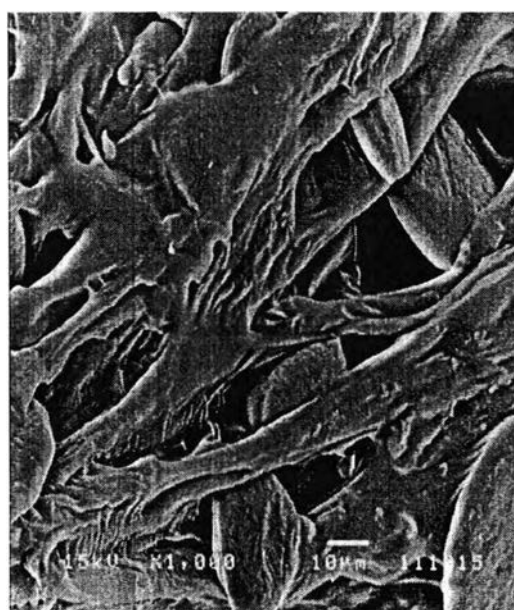
a) without triblock copolymer



b) with 5 wt % triblock copolymer

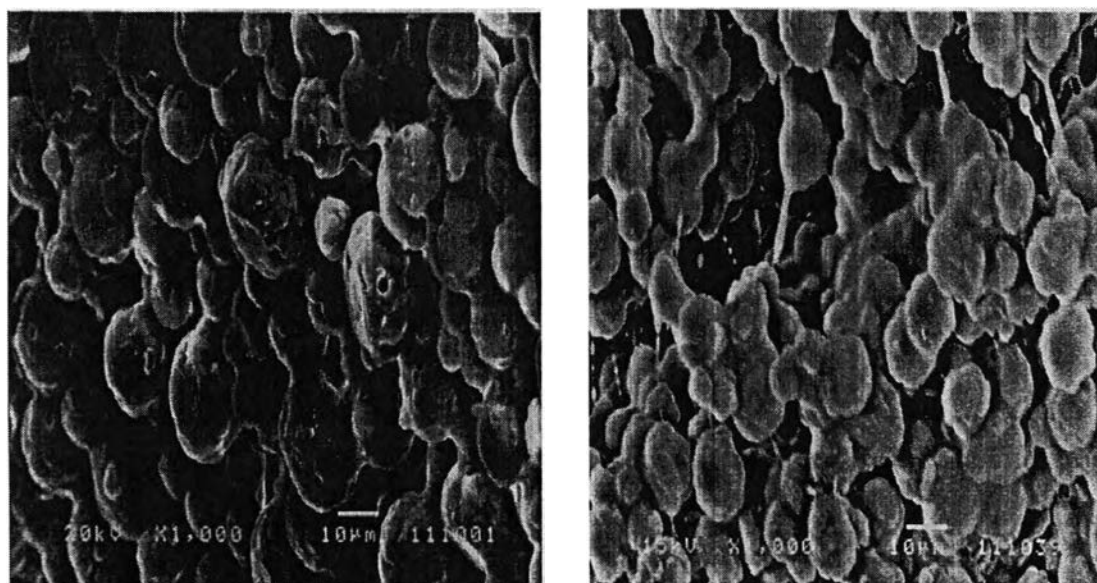


c) with 9 wt % triblock copolymer



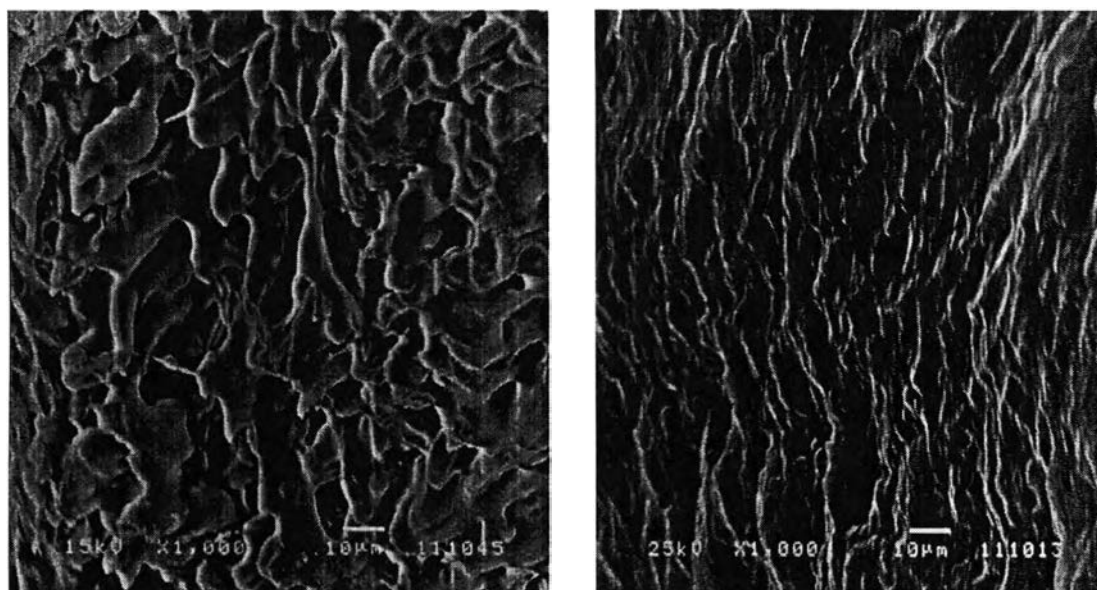
d) with 20 wt % triblock copolymer

Figure 3.12 SEM photographs of fracture surfaces of PS/PI-100 (40/60) blends: a) without triblock copolymer (x1000); b) 5 wt % triblock copolymer (x1000); c) 9 wt % triblock copolymer (x1000); d) 20 wt % triblock copolymer (x1000).



a) without triblock copolymer

b) with 3 wt % triblock copolymer



c) with 9 wt % triblock copolymer

d) with 20 wt % triblock copolymer

Figure 3.13 SEM photographs of fracture surfaces of PPO/PI-100 (40/60) blends: a) without triblock copolymer (x1000); b) 3 wt % triblock copolymer (x1000); c) 9 wt % triblock copolymer (x1000); d) 20 wt % triblock copolymer (x1000).

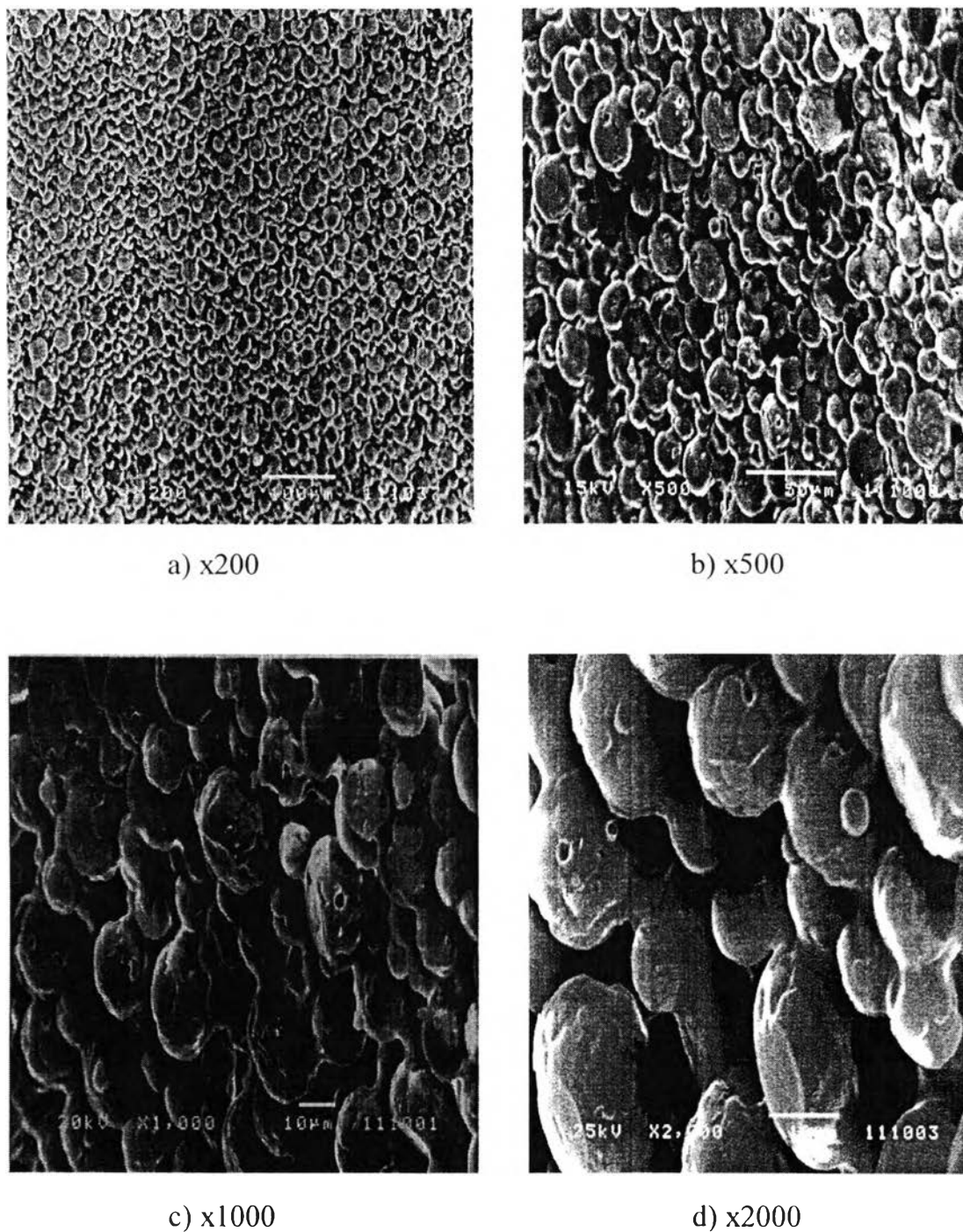


Figure 3.14 SEM micrographs of fracture surface of binary blend PPO/PI-100 (40/60) at various magnifications: a) x200 ; b) x500 ; c) x1000 ; d) x2000.