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Glass transition behavior of polypropylene/polystyrene/ styrene-ethylene-propylene block copolymer blends

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Summary

The glass transition behavior of ternary blends of polypropylene (PP), polystyrene (PS) and styrene-ethylene-propylene-styrene block copolymer (SEPS) was investigated. The blends were prepared by an internal mixer, and their dynamic mechanical properties and morphology were measured. The blends showed phase inversion at around 75wt% PS composition. The glass transition temperature (T_g) of the PP phase shifted to lower temperature as the PS contents were increased in PP/PS binary blends, probably due to the mismatch of thermal expansion coefficients between two components. As the SEPS copolymer contents were increased, the T_g's of the PP phase in the blends increased. In particular, the large increase in T_g of the PP phase was observed in the PP/PS (25/75) blends where the phase inversion takes place.

Introduction

The T_g of a polymer material is correlated with the segmental motion of the polymer chains. In the miscible polymer blends a single T_g is observed in the intermediate of the corresponding T_g of pure components depending on the composition. In the polymer blends with the phase separated structures, three types of T_g shift are reported.
1) No shifts from the corresponding parent polymers, which is generally observed in the completely immscible polymer blends (1,2).
2) Inward shifts toward the T_g of the other component polymer, which is generally observed in the partially miscible polymer blends with some degrees of intermixing occur (3).
3) Decreases in T_g of a soft phase observed in the rubber toughened plastics such as acrylonitrile-butadiene-styrene copolymer (ABS) and styrene-butadiene copolymer (4-8).

The reason for the lowering of the soft phase T_g has been explained in terms of the differences of thermal expansion coefficients between the hard matrix and the soft domain, resulting in the dilation of the soft phase due to the thermal stress.

In the previous paper (9), we have reported on the phase inversion behavior of PP/PS binary blends. The PP/PS blends revealed the phase inversion at the PS composition of around 75wt%, which results from higher melt viscosity of PS than that of PP. In the present report, the glass transition behavior, in particular, the T_g shift of the PP phase coupled with morphological changes of the PP/PS blends with SEPS component are described.

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Experimental

PP is commercially available as Hoprene J-150 from Honam. Petrochemical Co. (Korea). PS, Solarene G-144, was supplied by Dongbu Chemical Co. (Korea). SEPS block copolymer, Septon 2002, was purchased from Kuraray Co., Ltd. (Japan). A styrene content in Septon 2002 was 30 wt%. Physical properties of the polymers used in this study are given in Table 1.

An internal mixer (Haake Rheomix 600) fitted with roller blades was employed to prepare the blends. Pellets of PP, PS and SEPS were dry blended, added simultaneously and mixed at 60 rpm for 10 min at 210°C. The hot blends were removed from the mixer, rapidly cooled to room temperature. The SEPS was incorporated with 1, 2, 5, 10phr based on the total weights of the PP/PS blends. The blended samples were coded as P75/S25/C1 designating PP 75, PS 25 by wt%, respectively, and SEPS lphr.

The morphology of the PP/PS blends was investigated on compression molded samples. The specimens were obtained by fracturing in liquid nitrogen, and then the surface was coated with gold prior to viewing with a JEOL JSM-840A scanning electron microscope (SEM) operated at 20kV. Selective dissolution of SEPS was attempted with petroleum ether at room temperature.

Dynamic mechanical measurements were performed in a Rheometrics Dynamic Spectrometer (RD S-II) in the shear mode operating at a frequency 1 Hz and a constant strain 0.1%. The dimension of the testing sample was 40(L) x 12(W) x 2(T) mm. Nitrogen gas was circulated in the environmental chamber to minimize degradation during testing. The shear storage modulus, G', shear loss modulus, G", and loss factor, tan δ, were obtained at a heating rate of 3°C /min over the temperature range-150 °C to 200°C. The temperature that corresponds to a maximum in tan δ vs. temperature curves was considered the glass transition temperature, T_g, for the homopolymers and blended samples.

Table 1. Physical properties of the pure polymers

Polymer	$\overline{M}_n$ (g/mole)	$\overline{M}_w$ (g/mole)	Crystallinity[a] X_c(%)	T_g [b] (℃)	T_m [c] (℃)	PS content (wt%)
PP	55,400[d]	288,610[d]	47	6	162	-
PS	127,800[e]	220,200[e]	-	108	-	-
SEPS	23,800[e]	25,200[e]	-	-50	-	30

a) X_c is calculated with ⊿ H_{pp} = 209J/g (Ref. 10)

b) Temperature at tan δ maximum in RDS experiment

c) Peak temperature determined by DSC

d) Measured by gel permeation chromatography with PP calibration

e) Measured by gel permeation chromatography with PS calibration

Results and Discussion

Figure 1 shows the changes in the storage modulus and tan δ with temperature for the P75/S25/C blends with varying the SEPS compositions. At this composition, the PP forms the continuous phase and PS the dispersed phase. In Figure 1(a), it can be seen that the storage moduli of the P75/S25/C blends showed different shapes depending on the content of SEPS. Storage modulus of the P75/S25 blends shows two transitions at 4 and 100°C corresponding to the T_g's of PP and PS phase, respectively, and gradual decreases between the transitions. The storage modulus maintained a high value up to around 150°C where PP crystals begin to melt. The blends containing 1 and 2 phr SEPS also revealed the same trend as the P75/S25/C0 blend. However, the blends with SEPS above 5phr showed three transitions at -50, 0 and 100°C, large transition at -50°C and small transition at 100°C, implying that SEPS would forms a third phase due probably to exceeding the critical micelle concentration (CMC) for the interfacial agent. The same phenomena were observed in the plots of tan δ vs. temperature as shown Figure l(b). It can be seen that three well defined peaks were observed for the P75/S25/C blends regardless of the content of SEPS. In addition, at the content of SEPS above 5phr, peak height at -50°C remarkably increased and, on the contrary, the peak height at around 108°C corresponding to T_g of the PS phase were decreased.

Figure 2 shows the changes in the storage modulus and tan δ with temperature for the P25/S75/C blends with varying the SEPS compositions. For these blends with the PS rich composition the co-continuity morphology was observed even though PS is the major component, resulting from the low melt viscosity of PP compared to that of PS.

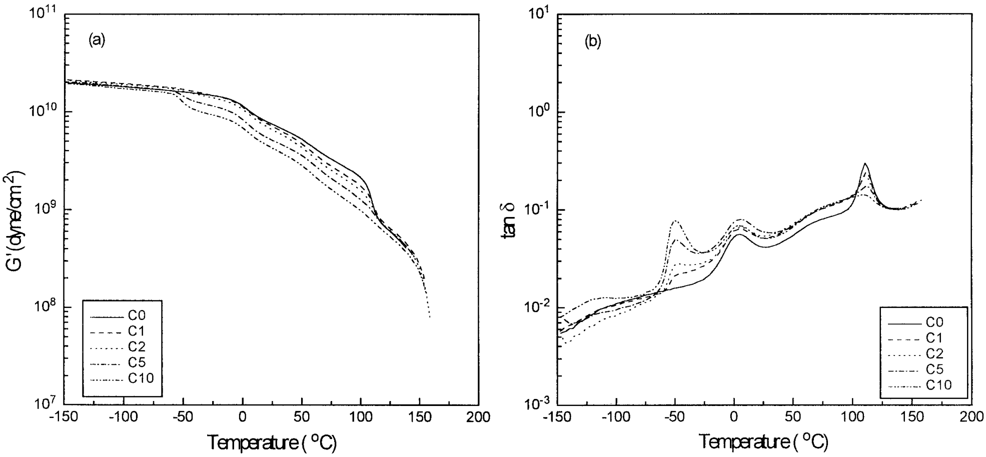

Figure 1. Dynamic mechanical properties of P75/S25/C blends: (a) storage modulus; (b) tan δ.

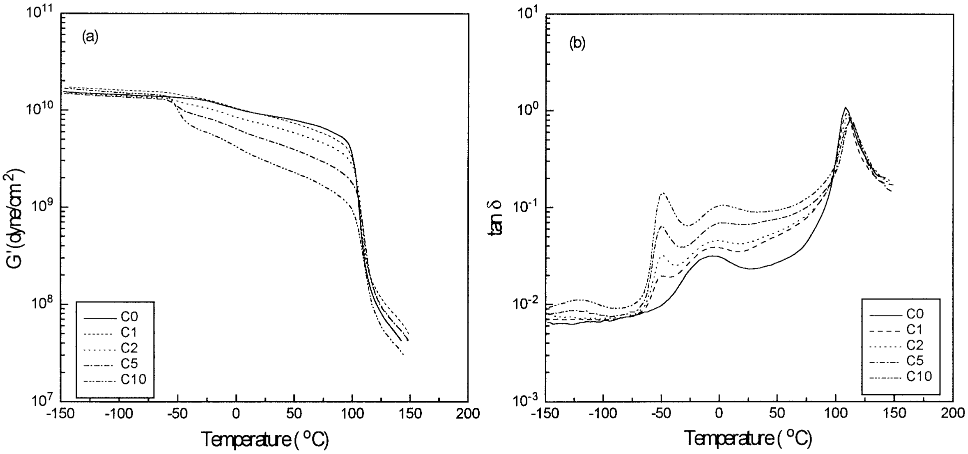

Figure 2. Dynamic mechanical properties of P25/S75/C blends: (a) storage modulus; (b) tan δ.

In Figure 2(a), the blends with less than 5phr SEPS retained high modulus up to 100°C, whereas the blends with above 5phr SEPS showed a sharp transition at around -50°C, and less gradual decrease in storage modulus with temperature was indicated compared to that of the P75/S25/C as shown in Figure 1 (a), which means the PS plays a major role in determining the modulus of the blends. From Figure 2(b), a similar trend to Figure 1 (b) in tan δ vs. temperature plots was noticed. It is worth noting that the maximum peak temperatures for the PP phase appearing at around 0°C were increased with increasing SEPS contents. This result will be discussed in detail in the last part of this paper.

Figure 3 shows the temperature dependence of storage modulus and tan δ for the P15/S85/C blend samples. In these blends, the PS forms the continuous phase and PP the dispersed phase. In Figure 3(a), the distinct transitions at around -50°C and 0°C corresponding to the T_g's of SEPS and PP phases, respectively, were not noticed for the P15/S85/C blends with up to 5phr SEPS. This reflects that the P15/S85 blends with 10phr SEPS has a third phase. In Figure 3(b), large peaks at around 100°C appeared due to the role of the major component, i.e. PS. And the peak height of PS phase showed very slight decreases whereas the peaks heights at -50°C and 0°C were increased distinctively with increasing the SEPS content.

The T_g changes of the PP phase in the PP/PS blends as a function of the SEPS content were summarized in Figure 4. The temperature that corresponds to a maximum in tan δ vs. temperature curve was considered the glass transition temperature, T_g, for the homopolymers and blend samples. In the PP/PS binary blends, the T_g of the PP phase was reduced from 6°C to -5°C as the content of the PS was increased over all the PS composition, that is, regardless of the matrix polymer. In most the rubber-plastic blends the decrease of T_g of a rubbery phase was observed when the rubber forms a dispersed phase. This results could be explained in terms of the negative pressure occurrence resulting from differential contraction due to the difference of the thermal expansion coefficients of the blend components upon cooling from the liquid state (5-8).

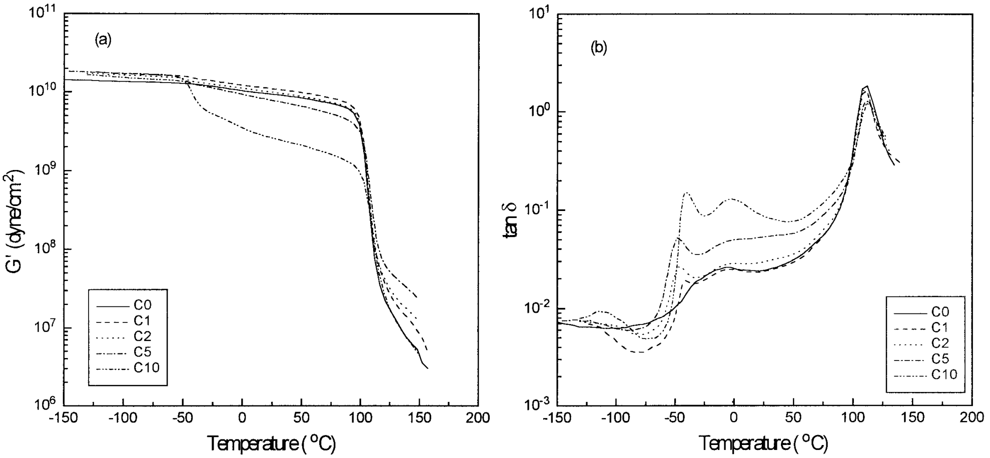

Figure 3. Dynamic mechanical properties of P15/S85/C blends: (a) storage modulus; (b) tan δ.

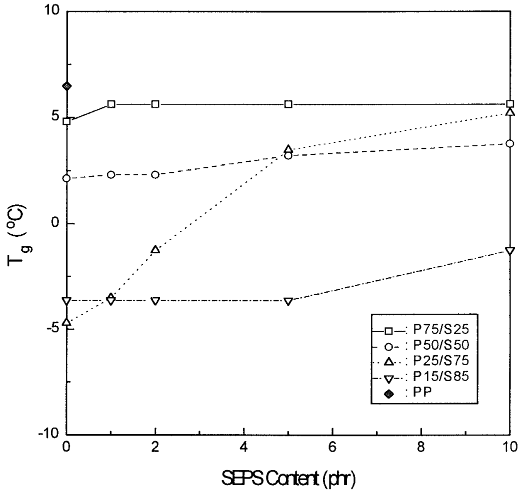

Figure 4. Changes in T_g of PP phase as a function of SEPS content.

As the temperature is cooled, the rubbery phase experiences a transition from the rubbery state to the glassy state at the glass transition temperature which accompanies the volume contraction. At this condition when the dispersed rubbery phase adheres very strongly to the hard matrix, the volume shrinkage of the rubbery phase was restricted due to the negative thermal stress, yielding the increase in the free volume of the rubbery phase compared to the neat state, which is attributed to the Tg shift to lower temperature for the rubbery phase. The PP/PS blends are assumed to consist of three phases of the amorphous and crystalline regions (X_c: 47% for this PP) in PP, and the glassy PS phase. Thus in the case of the PP rich blend, the hard region of the PP crystallite and the glassy PS phase can be speculated as major portion and the amorphous PP region which has high thermal expansion coefficient forms a dispersed phase. Thus the T_g of the amorphous PP region would shift to the lower temperature due to the mismatch between the hard matrix of PP crystallite, glassy PS and soft dispersed phase, as shown in Figure 4. For the blends which have the co-continuity morphology (P25/S75), it must be noted that the Tg of the PP phase was increased remarkably with increasing the SEPS content, which would results from the morphological change as shown in Figure 5. Figure 5 shows the morphology of the PP/PS/C blends containing 10phr SEPS. The compositions of PP/PS were P75/S25, P25/S75 and P15/S85. The SEM pictures were obtained for the fractured samples where the SEPS was selectively etched with petroleum ether. In the P75/S25/C10 blend, PP forms the matrix and PS aggregates appear as domains. This type of morphology could be attributed to the miscibility differences between the components. In ternary blends of A, B, and C, “domain in domain” morphology was reported by Hobbs et al(11). They explained as follows. When A is a continuous phase and B and C are dispersed phases, and in case the miscibility between A and B is lower than that between A and C, then C component would encapsulates B component, resulting in domain B in domain C.

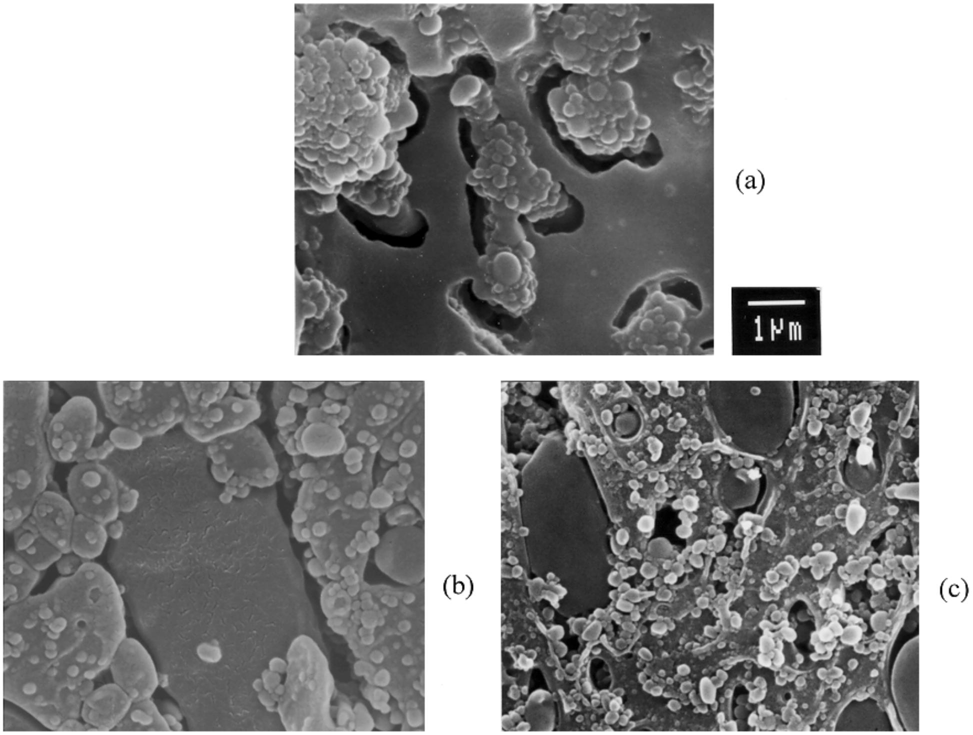

Figure 5. SEM micrographs of the PP/PS blends: (a) P75/S25/C10; (b) P25/S75/C10; (c) P15/S85/C10.

In our case of the P25/S75/C10 blend, the SEPS encapsulated the PS domains i.e., the very small sized PS phase (about 0.2μm) exists as domains in SEPS domains whereas the P25/S75 blend showed a co-continuity morphology as reported in the previous paper(9). This implies that the hard PS phase of the PP/PS blends is changed to the rubbery PS/SEPS phase at room temperature upon the addition of 10phr SEPS, which might reduce the thermal mismatch between the glassy PS phase and the rubbery amorphous PP phase. This morphological change is considered as the source of Tg shift in the PP phase to higher temperature as the rubbery SEPS content is increased. In the Pl5/S85/C10 blend, the PP forms a dispersed phase and the PS exists as a domain in SEPS matrix as revealed in Figure 5(c). Because the ratio of SEPS to PS content in the P15/S85/C10 is lower than that in the P25/S75/C10, the T_g. shift to the higher temperature appeared less remarkably for the P15/S85/C 10 than for the P25/S75/C10.

Conclusions

The blends of PP/PS showed phase inversion at around 75wt% PS composition. The T_g of the PP phase shifted to lower temperature as the PS contents were increased for the PP/PS binary blends probably because of the mismatch of the thermal expansion coefficients between the component polymers. As the SEPS copolymer contents were increased, the T_g of the PP phase in the blends was increased. In particular for the P25/S75 blends experiencing the phase inversion, the large increase in T_g. of the PP phase with the SEPS content was observed. This result has been explained in terms of the morphology change of the blends with the SEPS content.

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