

## The morphology and mechanical properties of the blends of syndiotactic polystyrene and polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene copolymers

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### Abstract

The morphology and mechanical properties of the blends of a syndiotactic polystyrene (SPS) and polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene copolymers (SEBS) with various polystyrene block contents are studied. Mechanical properties, especially elongation at break and impact strength (IS), of the blend depend upon the morphology and interfacial adhesion, which in turn are affected by the viscosity ratio of constituent components and the styrene block content in SEBS. The IS of a blend was affected by the combined effect of rubber content and the interfacial adhesion. A maximum IS was found for a blend with the weight fraction of the PS block in an SEBS of 0.18. The IS of blends with smaller weight fractions of the PS block exhibited lower due to poor interfacial adhesion between SPS/SEBS in spite of a larger amount of rubber block. On the other hand, the IS of blends with larger weight fraction of the PS block becomes smaller due to lower amounts of rubber block in spite of better interfacial adhesion.

**Keywords** : syndiotactic polystyrene, impact strength, polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene

### 1. Introduction

Syndiotactic polystyrene (SPS) with a very high degree of stereospecificity has successfully been synthesized by stereospecific polymerization [Ishihara *et al.* (1988)]. The advantages of SPS over commercially available engineering plastics are high heat resistance due to high melting temperature (>260°C), excellent chemical resistance, high degree of crystallinity, low specific gravity, good dielectric properties, and relatively fast crystallization rate [Cimmino *et al.* (1991)]. Because of these excellent properties of the SPS, it can be used as a material for electronics, automotive products, and industrial films. However, the brittleness and lower impact strength (IS) of SPS limit its use. The blending of SPS by an impact modifier would be one of methods for increasing the IS of SPS.

The morphology, thus mechanical properties, of polymer blends containing a copolymer as the compatibilizer is affected by the interfacial activity between the constituent components, which in turn strongly depends upon the chain architecture of the copolymer [Matos *et al.* (1995),

Char *et al.*(1993), Cigana *et al.*(1997)]. Both alternating and block copolymers efficiently strengthen the interface due to their extension along and/or across the interface compared with random copolymer. It is reported that the toughness, or impact strength, of a blend modified by a rubber particle depends upon particle size. For a polyamide and poly(ethylene-*ran*-propylene) rubber (EPR) blend system, the maximum toughness of polyamide was found at the rubber size of 0.2~0.3  $\mu\text{m}$  [Lazzeri and Bucknall (1993), Borggreve *et al.*(1989) and Oshinski *et al.*(1992)], while the toughening of polystyrene exhibits the best when the rubber size is 1~2  $\mu\text{m}$  [Bucknall (1997) and Kinloch and Young (1983)].

The choice of impact modifier for SPS is not easy due to high processing temperature of SPS. One of the candidates would be polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene copolymer (SEBS) exhibiting good thermal stability. SPS is miscible with atactic polystyrene (aPS), which was demonstrated by both enthalpy relaxation and crystallization kinetics or diffusion experiments [Hong *et al.* (1998), Bonnet *et al.* (1998), Ermer *et al.*(1997)]. Since the PS block in SEBS is miscible with SPS, the interfacial adhesion between SPS and SEBS might be good. Recently, Hong and Jo (2000) reported that lower molecular weight

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SEBS was more effective in increasing the impact strength of the blend of SPS and EPR when the PS block content is constant. They explained that the PS chains in low molecular weight SEBS penetrates more easily into the SPS phase compared with those in high molecular weight SEBS. The IS of a mixture is affected by the combined effect of rubber content and the interfacial adhesion. Thus, the IS of SPS toughened by SEBS depends not only on the total molecular weight of SEBS at given PS block content but on the block length ratio (or PS block content) in SEBS. In this study, we investigate the morphology and the mechanical property of toughened SPS by various SEBSs with different molecular weights and/or block length ratios.

## 2. Experimental

### 2.1. Materials

The SPS was kindly provided by Samsung Advanced Institute of Technology. The number-average and weight-average molecular weights ( $M_n$  and  $M_w$ ) were 200,000 and 400,000, respectively. From differential scanning calorimetry (Perkin-Elmer DSC-7 Series) thermogram, the glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of the SPS were 92.1°C and 250°C, respectively, measured at a heating rate of 10°C/min. Various commercially available SEBSs were used as an impact modifier of SPS. The molecular characterizations of SEBSs employed in this study are listed in Table 1.

### 2.2. Sample preparation and measurement

All of the polymers were dried under vacuum condition at 80°C for 2 days. The various blend compositions were prepared by using a MiniMax Molder at 290°C for 10 min. The maximum shear rate was 20 s<sup>-1</sup> and the total blend weight was 1 g. As soon as the blending was finished, molten samples were directly injected into a dog-bone shaped molder attached to the MiniMax Molder. The specimen dimension was 38 mm, 3.2 mm, and 4.7 mm (L×W×T) according to the ASTM D638. The tensile properties of specimens with various content of SEBS were obtained by using a universal tensile machine (Instron 4206) with a cross-head speed of 5 mm/min at room temperature. We also prepared an impact specimen with the dimension of 50

× 12.7 × 3.2 mm (L×W×T) according to ASTM D256 using the MiniMax Molder. Then, we made a notch in the specimens by using a notching cutter (TMI 22-01: Testing Machines Inc.). Izod impact strength was measured with an impact tester (TMI 43-1: Testing Machines Inc.) at room temperature.

### 2.3. Rheological measurement

Advanced Rheometrics Expansion System (ARES, Rheometrics Co.) using the dynamic oscillatory mode with parallel plate fixture of 25 mm diameter was employed to measure the complex viscosities ( $\eta^*(\omega)$ ) at wide ranges of frequencies ( $\omega$ ) and to determine order-disorder transition temperature ( $T_{ODT}$ ) of block copolymers. All experiments were done in nitrogen environment to exclude thermal degradation.

### 2.4. Morphological measurement

A Field Emission Scanning Electron Microscope (S-4200: Hitachi) was used to investigate the morphology of the blends after the specimens were carefully cut under liquid nitrogen atmosphere. In order to improve the phase contrast between two phases, the rubber phase in the specimen was etched out by cyclohexane with ultrasonic vibrator at 30°C for 20 min, and coated with a thin layer of gold. The number average ( $D_n$ ) domain sizes were obtained with a Quantimet 570 image analyzer (Cambridge Instruments) by using at least 200 domains. The cross-sectional area ( $A_i$ ) of each particle on the SEM micrograph was measured and then converted into the diameter ( $D_i$ ) of a circle having the same cross-sectional area:

$$D_i = 2(A_i/\pi)^{1/2} \quad (1)$$

Then,  $D_n$  was obtained by

$$D_n = \frac{\sum D_i}{N} \quad (2)$$

where N is the total numbers of dispersed domains seen in SEM image.

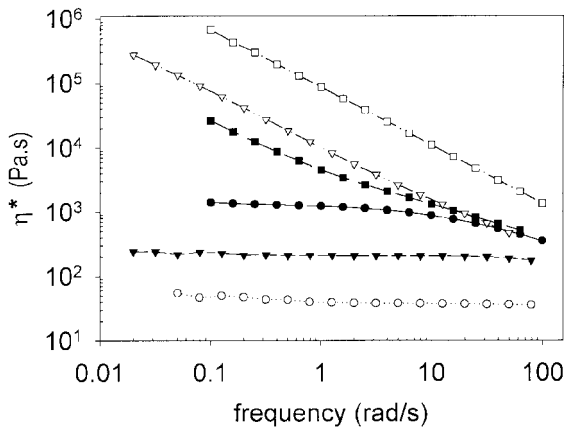
## 3. Results and Discussion

### 3.1. Rheological properties

Fig. 1 gives the complex viscosities ( $\eta^*$ ) of SPS and various SEBSs measured at 290°C. SPS and two SEBSs (SEBS-8 and H1062) showed newtonian behavior at lower frequencies ( $\omega$ ), while G1651, G1652 and H1043 have shear-thinning behavior. This implied that at the processing temperature of 290°C, G1652, H1043 and G1651 have microdomains, while SEBS-8 and H1062 are homogeneous. These are consistent with the results of the order to disorder transition temperature ( $T_{ODT}$ ) of these block copolymers measured by temperature sweep of G at  $\omega = 0.1$  rad/s and a heating rate of 1°C/min. For instance, the  $T_{ODT}$ s of

**Table 1.** Molecular characteristics of SEBS used in this study

Sample	Source	$M_w$ (g/mol)	PS block (%)	$M_{w,PS}-M_{w,PEB}-M_{w,PS}$ (Kg/mol)
G1651	Shell	174,000	33.3	29-b-116-b-29
G1652	Shell	51,500	27.2	7.0-b-37.5-b-7
H1062	Asahi	130,000	18	12-b-106-b-12
H1043	Asahi	84,000	67	28-b-28-b-28
SEBS-8	Asahi	67,000	8.8	3.0-b-61-b-3.0

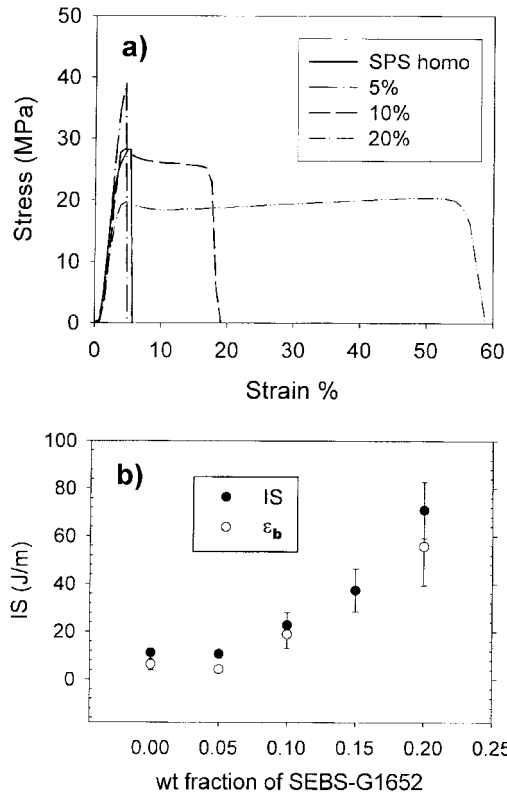


**Fig. 1.** The plots of complex viscosity versus frequency for SPS and SEBSs at 290°C. The strain amplitude was 0.05. (○) SEBS-8; (▼) H1062; (●) SPS; (■) G1652; (▽) H1043; and (□) G1651.

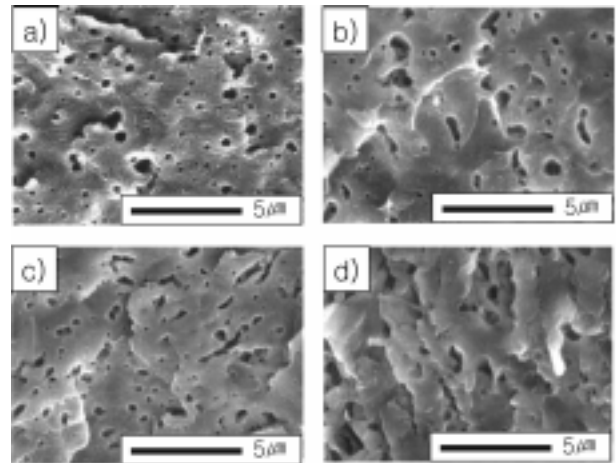
SEBS-8 and H1062 were 230 and 235°C, respectively, while the  $T_{ODT}$  of G1652 was ~315°C. It is noted, however, that the  $G$  of SEBS-8 decreased very much at the temperature of 150°C, which is the lattice disordering temperature [Kim *et al.* (1999)]. However, the  $T_{ODT}$ s of G1651 and H1043 were higher than 320°C, which was the limit of measurement to exclude any possible thermal degradation. The  $\eta^*$ s of H1043 and G1652 at  $\omega = 20$  rad/s, which is equivalent to the maximum shear rate of the processing condition in MiniMax molder on the basis of Cox-Merz rule, are similar to that of SPS due to shear thinning effect. But, the  $\eta^*$  at  $\omega = 20$  rad/s of G1651 and H1062 were one order of magnitude higher and lower, respectively, than that of SPS. Furthermore, the  $\eta^*$  of SEBS-8 is two orders of magnitude lower than that of SPS. These rheological properties are important in explaining the morphology since the morphology of a blend is strongly affected by the viscosity ratio of the dispersed phase to that of the matrix [Shonaike *et al.* (1998)].

### 3.2. Tensile and Izod Impact properties

Fig. 2(a) shows tensile stress versus tensile strain curves for various SPS/G1652 blends. As expected, with increasing amount of SEBS, the blend became more ductile. A sharp increase of elongation at the break ( $\epsilon_b$ ) was observed when the amount of G1652 was 10%, and the  $\epsilon_b$  of a blend with 20 wt % of G1652 increased up to ~60%. It is seen in Fig. 2(b) that the trend of the increase in IS was the same as that in  $\epsilon_b$ . But, in spite of a large increase in IS and  $\epsilon_b$ , Young's modulus ( $E$ ) decreased much. For instance,  $E$  of a blend with 20 wt % of G1652 was decreased about 30% compared with that of neat SPS. This lower  $E$  might limit the use of SPS for an advanced material. Thus, the proper design of another blend system exhibiting higher IS, but without sacrificing  $E$ , is utmost needed. One such direction



**Fig. 2.** (a) Tensile stress and tensile strain curves at various blend compositions of SPS/G1652 system. (b) The change in impact strength and elongation at break with blend composition for SPS/G1652 blend system.



**Fig. 3.** SEM images of SPS/G1652 blend system. The blend composition of G1652 (wt %) was (a) 5; (b) 10; (c) 15; and (d) 20.

might be to use poly(2,6-dimethyl-1,4 phenylene oxide) (PPO) [O(2001)].

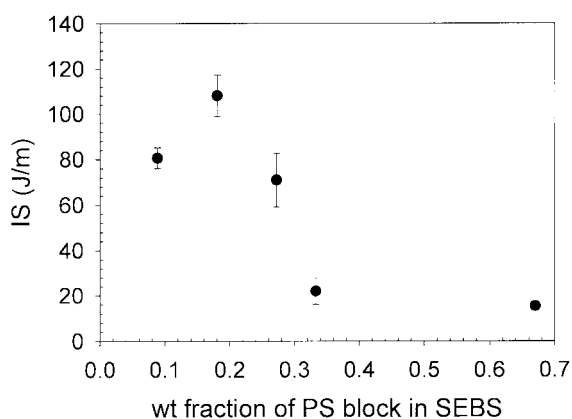
Fig. 3 gives the SEM images of various blends of SPS/G1652, showing fine dispersion of G1652 in SPS. However, this domain size is much larger than hexagonally

packed cylindrical (HEX) microdomains of the PS block in G1652 itself (27 nm) [Kim *et al.* (2000)]. Thus, the dispersed microdomains represent SEBS-rich (or pure SEBS) phases within which HEX microdomains of PS block are formed. It is seen in Fig. 3 that the domain size of dispersed G1652 domain increases with increasing amount of G1652, although the increase is not large. A blend with 20 wt% of G1652 has still fine dispersion of SEBS-rich phases in SPS. Thus, the increase in IS with G1652 is mainly due to the increase amount of rubber content, rather than the increase of rubber domain size.

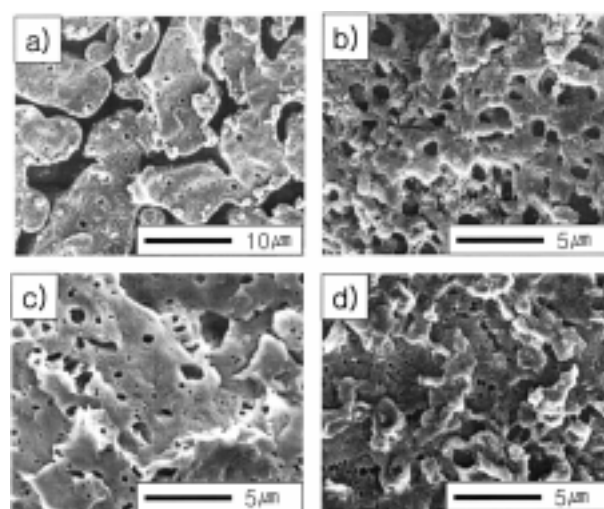
### 3.3. Izod Impact strength of SPS/SEBS blends with various kinds of SEBS

As shown earlier, the IS depends upon the structure of block copolymer (SEBS) as well as the interfacial adhesion. In order to increase toughness (ductility) of the blend, the rubbery block should be increased. However, in this situation, the PS block in SEBS should be shortened, which implies that the interfacial adhesion between SPS/SEBS would be worse. On the other hand, a blend with smaller rubber content gives a poor IS due to lower amount of rubber phase. Thus, it might have an optimum PS block content exhibiting the maximum IS when the added amount of SEBS is constant.

Figs. 4 and 5 give the IS variation and SEM images, respectively, with the amount of PS block when the amount of SEBS is constant (20 wt%). First we consider the difference in IS between G1651 and G1652 blend systems, where the IS of 80/20 (wt/wt) SPS/G1651 blend was twice lower than that of 80/20 (wt/wt) SPS/G1652 blend. This is due to the morphology difference between two blend systems, namely, the dispersion of G1651 domains in the matrix was very poor (compare Fig. 3 with Fig. 5). The larger domains size in G1651 in SPS/G1651 blend compared with that of G1652 in SPS/G1652 blend is attributed to the large difference in viscosity between constituent



**Fig. 4.** Izod impact strength of 80/20 (wt/wt) SPS/SEBS blends with various PS block ratios.



**Fig. 5.** SEM images of 80/20 (wt/wt) SPS/SEBS blends: (a) SPS/SEBS-8; (b) SPS/H1062; (c) SPS/G1651; and (d) SPS/H1043.

components for the former system (see Fig. 1). Since  $M_w$  of SPS is 400,000, which is much larger than the molecular weight of PS block in either G1651 or G1652, the ability of the SPS chain to enter a block layer (namely wet brush) is not expected. In this situation, we must consider the degree of entanglement of SPS chains with PS chains of SEBS located only at the boundary of the SEBS-rich dispersed domains. The entanglement of two chains is mainly determined by the interdiffusion of SPS into PS chains (or vice versa). Since the viscosity of G1651 is ten times larger than that of G1652 at the processing condition, the diffusion of PS chains in the former into SPS at a given processing time is more difficult. Also, because the  $T_{ODT}$  of G1651 is larger than that of G1652 (also larger than the processing temperature), PS chains in G1651 are easily formed into HEX domains in SEBS-rich dispersed phase at this processing temperature; thus the amount of PS chains locating at the boundary of G1651-rich dispersed phase, which plays the entanglement with SPS chains, is smaller than that for G1652. Thus, we conclude that even if the PS chains of G1652 are smaller than those of G1651, the former blend exhibits higher IS.

However, it is seen in Fig. 1 that as frequency is further increased, the viscosity of G1651 decreased rapidly due to its high non-newtonian nature. Thus, it would be interesting to investigate whether or not IS of SPS/G1651 blend becomes similar (or even higher) than that of SPS/G1652 blend if a fine dispersion of G1651 in SPS, which is similar SEBS-rich domains size with G1652/SPS system, is obtained through a better mixing device (Brabender Mixer or twin screw extruder). Unfortunately, we could not test this possibility due to a limit amount of SPS.

It is seen in Fig. 4 that even though the total molecular

weights of SEBSs employed in this study are different, one might consider that the maximum IS was found at the blend with the PS block of 18 wt %. However, as shown in Fig. 5 that the dispersed domain sizes generally decreased with increasing PS block in SEBS. For the SPS/SEBS-8 blend, even though the amount of rubbery phase (PEB) is the largest, the impact strength is lower than SPS/H1062. This is because the molecular weight of the PS chain in SEBS-8 is too small to make enough entanglement with SPS chain. Furthermore, the viscosity difference between SEBS-8 and SPS was two orders of magnitude. This was clearly seen in SEM image given in Fig. 5 that the dispersed phases of SEBS-8 are too large and poor dispersion. On the other hand, the domain size for SPS/H1043 blend became very small (0.1~0.3  $\mu\text{m}$ ) due to large amount of PS block, but the amount of the rubber content became too small to exhibit higher IS. It has been reported that rubbers with their domains below 0.2~0.3  $\mu\text{m}$  give little contribution to the IS of amorphous PS toughened by rubber [Burknall (1997)]. SPS/H1062 blend gives the domain size of 1~2  $\mu\text{m}$ , which would be the best size for optimum toughening of SPS. It is known that rubber-toughened amorphous PS has a maximum toughness when the size of the dispersed rubber phase is 1~2  $\mu\text{m}$  [Bucknall (1997) and Kinloch and Young (1983)]. Furthermore, since the  $T_{\text{ODT}}$  of H1062 is 235°C, the lots of PS chains could participate easily to entangle with SPS chains at the processing temperature. Finally, the IS of blends might depend upon the tensile modulus (E) of an impact modifier itself. As long as the interfacial adhesion is similar, the lower E, the higher IS, because an impact modifier with lower E is easy to release the external stress. We found that E of H1062 is half of that of G1652, while E of G1652 is again half of that of G1651. Thus, one reason why the IS increases with decreasing PS block in SEBS in the range of the weight fraction of PS block larger than 0.18 is due lower modulus of SEBS itself.

#### 4. Conclusions

In this study, we have shown that the PS block ratios and the total molecular weights of SEBS affected significantly morphology and the impact and tensile properties of SEBS-toughened SPS. Blending of SPS by SEBS is a method for increasing the impact strength of SPS. The maximum impact strength was observed when SPS was blended by H1062 (18 wt % PS block) and the dispersed domain size of SEBS-rich phase for this blend was 1~2  $\mu\text{m}$ .

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