

Optical Transparency, Thermal Resistance, Intermolecular Interaction, and Mechanical Properties of Poly(styrene-butadiene-styrene) Copolymer-Based Thermoplastic Elastomers

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ABSTRACT: The optical transparency, thermal resistance, intermolecular interaction, and mechanical properties of poly(styrene-block-butadiene-block-styrene) (SBS), which were modified by blending with crystalline polypropylene (PP) or amorphous polystyrene (PS), were analyzed. The dynamic mechanical test indicated that the PP exhibited an intermolecular interaction with SBS and PS was compatible with SBS. The optical properties indicated that the direction of the light was changed due to the difference between the refractive indices of SBS and the added modifiers. Additionally, refraction and reflection

occurred at the interface, reducing the transparency of SBS. The thermal resistance of SBS clearly improved upon modification by the addition of crystalline PP polymer. The thermal treatment increased the tensile strength and the elongation at breakage of modified SBS by reducing the internal stress, which was generated during the blending process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 172–178, 2010

Key words: thermal resistance; SBS; PP; PS; refractive index

INTRODUCTION

Blending is the process of mixing two or more polymers in various proportions to attain a desired performance.^{1–3} One of the primary advantages of blending is its simplicity, as it depends on common equipment and technology,^{4,5} and various components that have predictable physical and chemical properties, which facilitates the evaluations of the properties of the mixture.^{6,7} Poly(styrene-block-butadiene-block-styrene) (SBS), a commercial thermoplastic elastomer, is very important because of its ease of processing and unique characteristics that are similar in many ways compared with those of a conventional vulcanized rubber. The uses of crystalline polypropylene (PP) and amorphous polystyrene (PS) to modify SBS have been investigated to improve the performance of SBS.

Saroop and Mathur^{8–10} investigated the mechanical and rheological properties, and the crystalline structure of PP in vulcanized SBS/PP blends that contained up to 40 wt % of SBS. Halavata et al.¹¹ examined the crystalline structure of PP in blends

with several thermoplastic elastomers. Gallego et al.^{12,13} analyzed the morphology of SBS blends with various PP contents and the improvement in their mechanical properties. Perera et al.¹⁴ investigated the effects of gamma radiation on PP, SBS, and PP/SBS blends. Ichazo et al.¹⁵ compared the rheological and mechanical behaviors of dynamically and statically vulcanized PP/SBS blends. Sanchez et al.¹⁶ examined the reinforcing effect of a dispersed phase of PS on the mechanical properties of an SBS triblock copolymer. Jelcic et al.¹⁷ analyzed the mechanical properties and fractal morphology of SBS/PS blends that contained up to 85 wt % SBS elastomer. Boyanova et al.¹⁸ evaluated the phase boundary in PS/SBS blends by microindentation analysis. Mohammady et al.¹⁹ investigated the relaxation behavior of the glass process of the PS/SBS blends.

Although SBS/PP and SBS/PS blends have been investigated intensively, no work on the optical transparency and thermal resistance of these blends, which are important properties in some applications (such as footwear) has been published. Therefore, the effects of PP and PS on optical transparency, heat shrinkage, intermolecular interaction, and mechanical properties, with and without thermal treatment of the modified SBS blends are investigated in this study.

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EXPERIMENTAL

Materials

The polymers, herein, were SBS radial copolymers (Grade: TPE475) (LCY Chemical Industry, Taiwan) with a styrene content of 40%. The PP (Grade: PT331M) was obtained from Taiwan Polypropylene, Taiwan and the PS (Grade: PG383) was obtained from Chi Mei, Taiwan. Table I presents the relevant characteristics of SBS, PS, and PP.

Sample preparation

SBS/PP and SBS/PS blends (Table II) were prepared from the melt blending pellets of both components in a twin-screw extruder (Werner and Pfleiderer, Model-ZSK 26 MEGAcompounder). Extrusion was performed at a screw rate of rotation at 500 rpm and a temperature of 200–220°C. The extruded thread was then pelletized. These blended pellets were then injected into 2-mm-thick molds.

Measurements of optical properties

Haze value (H) and the total light permeation coefficient (T) were measured by a Haze/Turbidimeter (Nippon Denshoku Industries, Japan, Model No. NDH 2000), according to the ISO 13,468 and ISO 14,782 methods. The refractive index was measured using an ABBE-refraktometer (KRUSS, Germany, Model No. AR 2008), according to the ASTM D1218 method. Thermal treat was performed in an oven at 100°C for 5 min.

Thermostability measurements

The heat shrinkage of each 2-mm thickness specimen (ASTM D412 Die C) was determined. The original length (L_0) of each was 115 mm. A specimen was placed into the thermal cabinet at 115°C for 10 min without any stress and the final length (L_f) was measured. Five measurements of each specimen were made and the results averaged to obtain a

TABLE I
Characteristics of Polymers Used as
Reported by Producers

Polymer	Melt flow index (g/10 min)	Heat distortion temp. (°C)
SBS	4.5 ^a	–
Polypropylene	14.5 ^b	122
Polystyrene	2.2 ^b	100

^a At 190°C, 5 kg.

^b At 200°C, 5 kg.

TABLE II
Compositions of SBS/PP and SBS/PS Thermoplastic
Elastomers

	Materials (phr)		
	SBS	PP	PS
SBS	100	–	–
SBS/PP20	100	20	–
SBS/PP40	100	40	–
SBS/PP60	100	60	–
SBS/PP80	100	80	–
PP	–	100	–
SBS/PS20	100	–	20
SBS/PS40	100	–	40
SBS/PS60	100	–	60
SBS/PS80	100	–	80
PS	–	–	100

mean value. Heat shrinkage was calculated by the following equation;²⁰

$$\text{Heat shrinkage} = (L_0 - L_f)/L_0 \times 100\%$$

Measurements of dynamic mechanical properties

Dynamic mechanical data were obtained using a dynamic mechanical analysis (DMA) instrument (TA Q800) with the following parameters: frequency 1 Hz, scan rate 5°C/min, and temperature range from –100 to 130°C.

Measurements of mechanical properties

Tensile strength and elongation at breakage were measured using a Universal Tensile Tester with a tension velocity of 500 mm/min based on ASTM D412C specifications.²¹ Thermal treat was performed in an oven at 100°C for 5 min. Five measurements of each specimen were made and the results averaged to obtain a mean value.

Morphological analysis

Morphology was evaluated using a JEOL JSM6360 Scanning Electron Microscope (SEM). A gold pattern was sputtered onto the sample fractured surface, and an SEM was used to examine the sample.

RESULTS AND DISCUSSION

Optical properties

Figure 1 presents the refractive index of SBS, PP, PS, SBS/PP, and SBS/PS blends at 30°C. The refractive indices of PP and PS greatly differed from that of SBS. Consistent with the studies of Maruhashi and Iida²² and Khanarian,²³ most analyses of the optical

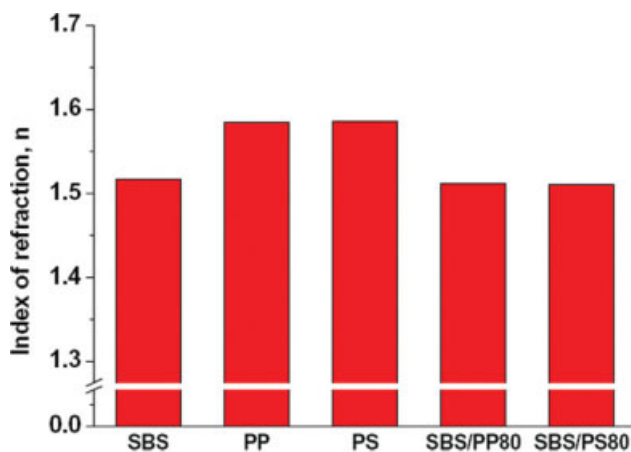


Figure 1 Refractive indices of SBS, PP, PS, SBS/PP, and SBS/PS blends at 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

properties of plastic composites have been guided by the following two observations: (1) small particles scatter more light than large particles and (2) decreasing the refractive index contrast between a particle and the surrounding matrix reduces the amount of light scattered by a particle. These principles demonstrate that after SBS has been blended by PP (or PS), the light that passes through the composites will pass through air/SBS and SBS/PP (or PS) interfaces, causing refraction and reflection because the SBS and PP (PS) have different refractive indices.

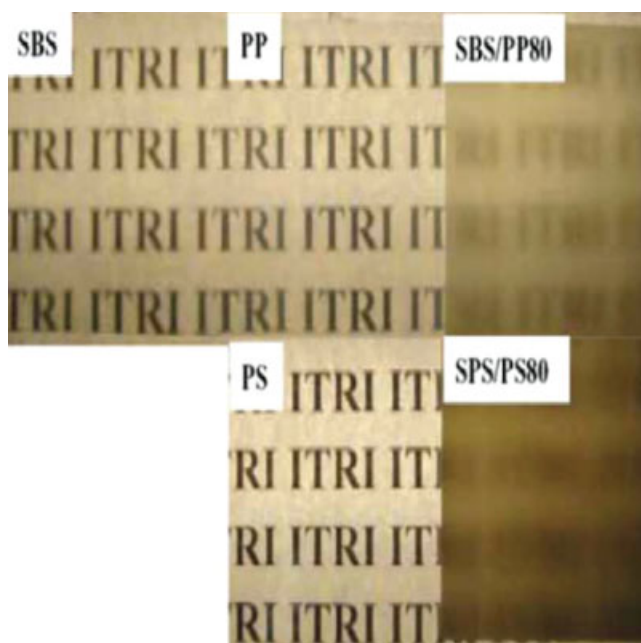


Figure 2 Transparency effects on SBS elastomers modified by PP and PS (2-mm thick). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Light is scattered due to the difference between refractive indices, and the reflection decreases the light permeation coefficient. Therefore, extensive refraction and reflection caused the SBS/PP and SBS/PS blends to lose its translucent properties, as shown in Figure 2.

Table III presents the haze values (H) and total light permeation coefficients (T) of PP, PS, SBS, SBS/PP, and SBS/PS blends with various compositions. Materials with a low H value (high transparency) generally have a high T value, but the reverse is not true. For example, diffused materials, which are hazy and are used in display back-light modules, have a high light permeation coefficient. Similarly, SBS belongs to a group of materials with a high H value of about 95% and a high T value of about 81%. Because the styrene hard segment exhibits physical cross-linked domain (phase separation) in SBS, scattering, light permeability, and diffused effects are generated. PP was the crystalline polymer whose H value and T value were about 50% and 78%. Amorphous PS polymer had a high T value of about 88% and a low H value of about 3%. Furthermore, when PP and PS modifiers were mixed into the SBS matrix, the H value increased to 99%, which indicates that the light passed through the blends caused reflection and diffusion. The T value decreased as modifier was content increased, as shown in Table III.

The optical properties of these samples after thermal treatment (at 100°C for 5 min) were also studied. Observations indicated that thermal treatment did not change H value but slightly increased the T value of the SBS/PP blend, probably because of the release of the stress residual following thermal treatment. However, T value continued to decrease

TABLE III
Optical Properties of SBS Elastomers Modified by PP and PS (Thickness, 2 mm)

	Before thermal treatment		After thermal treatment (100°C × 5 min)	
	T (%)	H (%)	T (%)	H (%)
SBS	81.03	95.26	86.71	95.83
PP	78.32	50.78	77.27	52.83
SBS/PP20	53.82	99.28	56.24	99.24
SBS/PP40	50.81	99.37	52.91	99.35
SBS/PP60	49.74	99.36	51.55	99.34
SBS/PP80	48.06	99.36	48.98	99.35
PS	88.25	3.36	89.47	8.81
SBS/PS20	20.42	99.32	18.88	99.33
SBS/PS40	16.68	99.35	12.45	99.33
SBS/PS60	14.33	99.36	10.30	99.30
SBS/PS80	13.28	99.32	9.11	99.21

T = total light permeation coefficient; H = Haze.

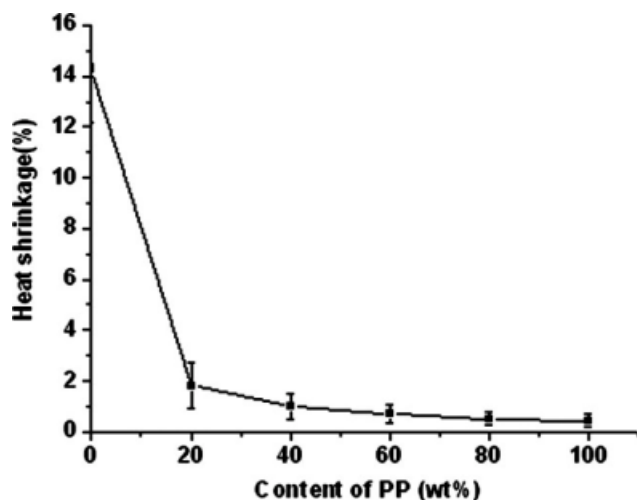


Figure 3 Thermal stability of SBS/PP blends elastomers with various amounts of PP.

following the thermal treatment of the SBS/PS blend, indicating that thermal treatment enhanced the interface effects and increased the reflection of the light that passed through the SBS/PS blends.

Thermostability

Figures 3 and 4 present the heat shrinkage of PP- and PS-modified SBS, respectively. The heat shrinkage was about 14% for SBS, 0.4% for the PP polymer, and 18% for the PS polymer. The experimental data from Figure 3 indicated that the heat shrinkage of the SBS/PP blends depended on PP content. The heat shrinkage decreased from 14% (for SBS) to a mere 1.8–0.5% (for SBS/PP blends), possibly because of the excellent thermal resistance of the crystalline PP. Therefore, combining PP with SBS effectively

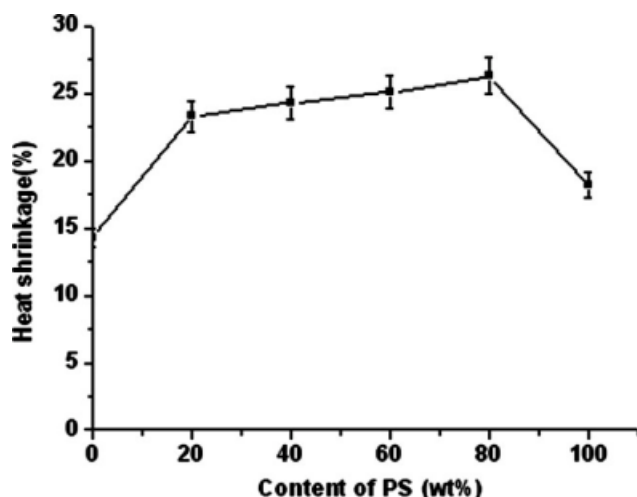


Figure 4 Thermal stability of SBS/PS blends with various amounts of PS.

improved the SBS thermal resistance by a factor of 10. When SBS was modified by adding various amounts of PS, heat shrinkage remained increased in the range of 23–26% as the PS content increased, as presented in Figure 4. These experimental results showed that SBS/PS blends shrank more than neat SBS or PS, perhaps, because of the compatibility of SBS and PS.

DMA analysis

The aggregate structure of a polymer blend can be determined by the intermolecular interaction with DMA.^{24–26} Figures 5 and 6 present DMA profiles of various blends measured at 1 Hz. These profiles showed that SBS yields two characteristic peaks, one at the glass transition temperature (T_{g1}) of the butadiene block in SBS about -69.7°C , and the other at the glass transition temperature (T_{g2}) of the styrene block in SBS about 96.3°C . The glass transition temperature ($T_{g\alpha}$) of the PP polymer was about 21.8°C . The glass transition temperature ($T_{g\beta}$) of the PS polymer was about 123.7°C .

From SBS/PP blends, for example, three characteristic peaks of SBS/PP80 at -84.1°C (SBS butadiene block), 0.6°C (PP), and 88.5°C (SBS styrene block) were observed. The temperatures of these characteristic peaks were lower than those of neat SBS and PP polymer. The temperature difference between the SBS/PP blend and neat polymers were 15°C for SBS butadiene block, 8°C for styrene block, and 21°C for PP, as presented in Figure 5. These results indicated that a loose aggregate structure formed in the SBS/PP in which PP, SBS butadiene, and SBS styrene blocks could slip intermolecularly. Therefore, the

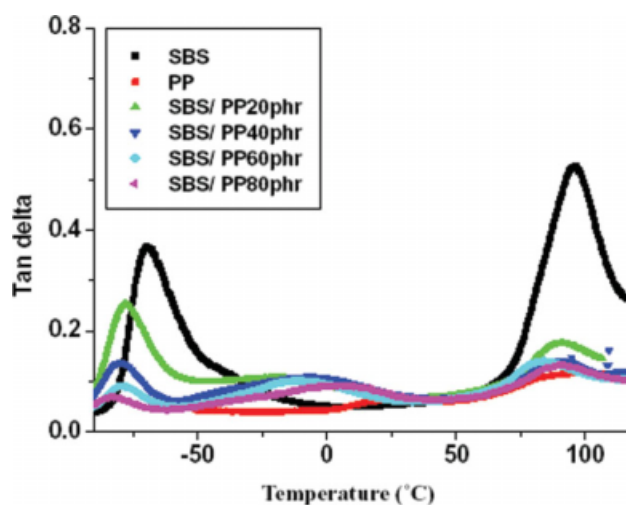


Figure 5 DMA curve of SBS/PP blends with various amounts of PP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

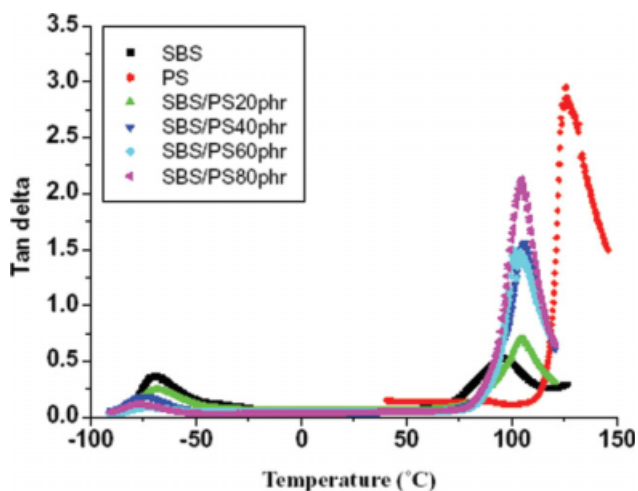


Figure 6 DMA curve of SBS/PS blends with various amounts of PS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

characteristic peaks of SBS and PP shifted toward the low-temperature region.

DMA measurements of SBS/PS blends revealed two characteristic peaks: the peak at a low temperature corresponded to the SBS butadiene block and the peak at a high temperature for the mixture of PS polymer and the SBS styrene block. The temperature of the characteristic peak of the SBS butadiene block decreased to -78°C , which effect was similar to that of SBS/PP blends. Furthermore, the PS polymer and SBS styrene block exhibited good miscibility, shifting the characteristic peak of the styrene block toward the high-temperature region and the characteristic peak of PS polymer moved toward the low-temperature region such that a single characteristic peak was observed at 104.6°C , as presented in Figure 6.

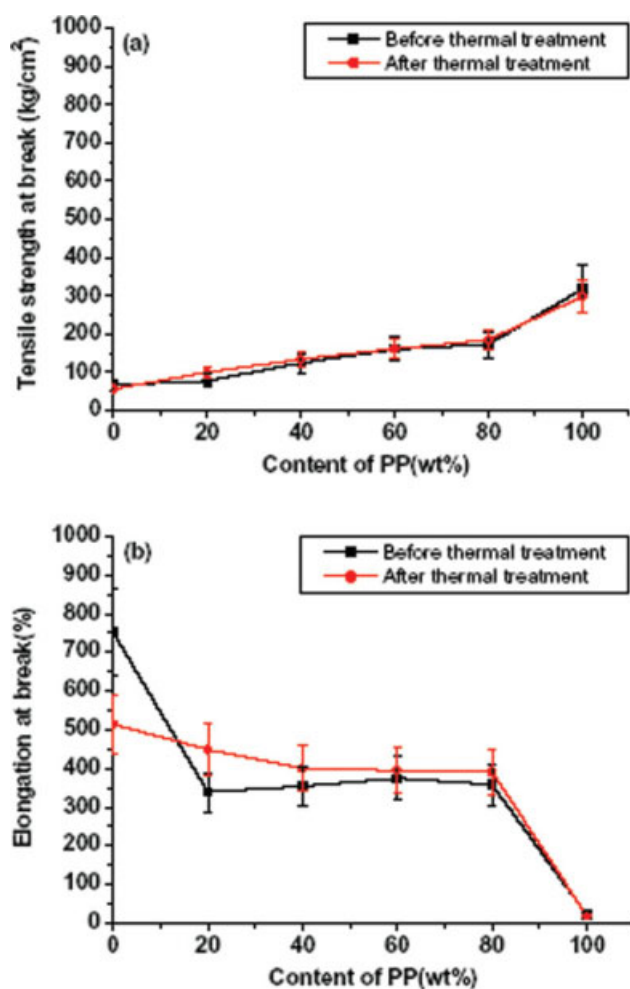


Figure 7 (a) Tensile strength and (b) Elongation of SBS/PP blends with various amounts of PP (before and after thermal treatment). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

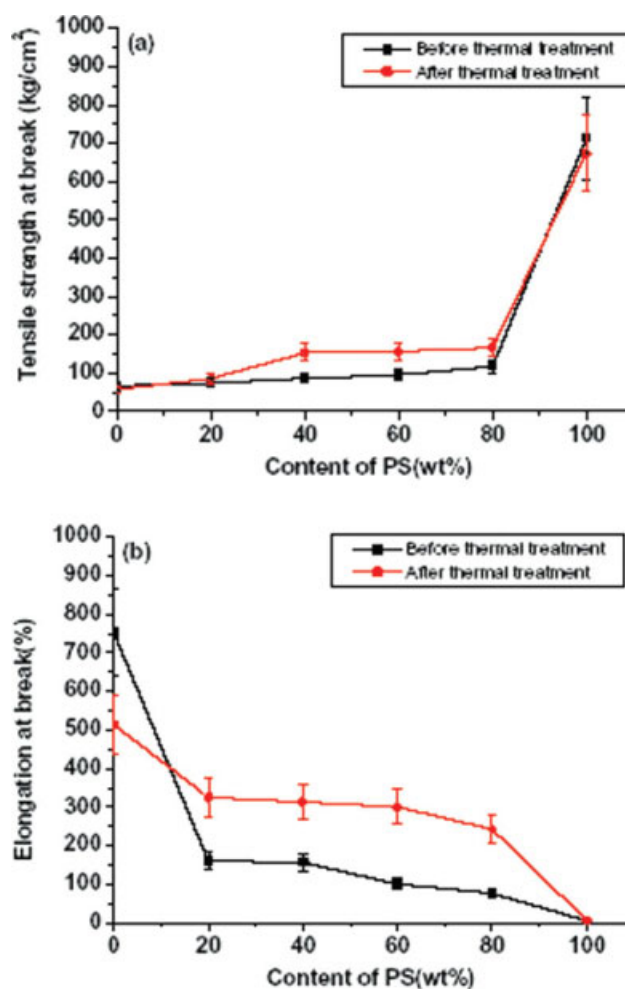


Figure 8 (a) Tensile strength and (b) Elongation of SBS/PS blends with various amounts of PS (before and after thermal treatment). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

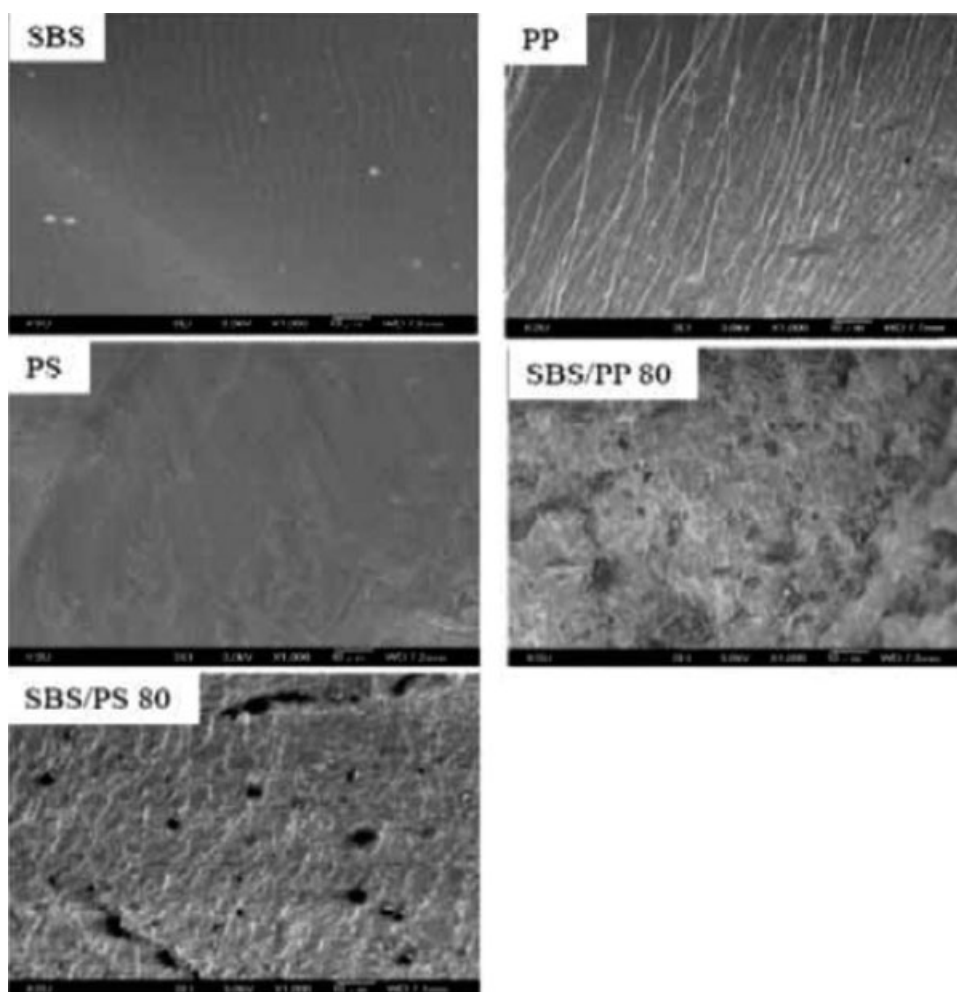


Figure 9 SEM of the fractured surfaces of SBS, PP, PS, SBS/PP, and SBS/PS blends.

Mechanical properties

The mechanical properties of SBS modified by PP and PS, which were measured before and after thermal treatment at 100°C for 5 min, are presented in Figures 7 and 8, respectively. SBS is an elastomeric material with remarkable elongation (about 752%), whereas PP and PS exhibit excellent tensile strength; however, their elongations are only 23% and 6%. Thermal treatment reduced the elongation at breakage of SBS by about 32% by thermally oxidizing the unsaturated butadiene block in SBS, which caused chain scission of SBS. However, no significant change in the mechanical properties of neat PP and PS was observed.

The tensile strength at the breakage of SBS blends increased with the PP and PS contents, as presented in Figures 7(a) and 8(a). The elongation at breakage of these blends decreased with the addition of PP and PS polymers, as presented in Figures 7(b) and 8(b). Thermal treatment improved the tensile strength and the elongation of SBS blends. These results revealed that thermal treatment released the

internal stress which was generated during blending.²⁷ Thermal treatment improved the mechanical properties of SBS/PS blends more than it did those of SBS/PP blends, perhaps, because the PS dispersed phase created more internal stress than the PP dispersed phase during blending.

Morphological analysis

Figure 9 shows the fractured surfaces of SBS, PP, PS, SBS/PP, and SBS/PS blends, which were produced by stretching. The fractured surface of SBS was light-colored and wave-like lines. PP had a fractured surface with many white lines which were formed by the strain-induced crystallization during stretching, indicating that PP was destroyed by plastic extension. However, the fractured surface of PS was not neat and revealed that its brittleness caused no plastic extension occurred.

In SBS blends, successive white regions and certain particles were observed in the fractured segments, indicating that the PP and PS modifiers were

equally dispersed in the SBS matrix. Moreover, the number of particles in the unit area of SBS/PS blends exceeds that in SBS/PP blends whereas those in SBS/PS blends were smaller in SBS/PP blends, indicating that SBS acted as a compatilizer in SBS/PS blends.

CONCLUSION

In this study, the effects of crystalline PP polymer and amorphous PS polymer as modifiers on the physical properties of the SBS matrix were studied. The dynamic mechanical test showed that the PP interacted intermolecularly with SBS, and PS was compatible with SBS. The thermal resistance of SBS materials clearly improved, when SBS was modified with crystalline PP polymer. However, the transparency of SBS was reduced when PP and PS were added, because the refractive index of the SBS matrix differed from that of the added modifiers. Additionally, following thermal treatment, the mechanical properties of modified SBS can be improved by releasing the internal stress that was generated during the blending process.

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