

Behavior of Ionomers of Sulfonated Styrene–Butadiene–Styrene Triblock Copolymer in Polymer Blends with Crystalline Polyolefins and as Compatibilizer

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ABSTRACT: The blends of ionomers of sulfonated (styrene–butadiene–styrene) triblock copolymer with two polyolefins as well as the blends of polystyrene (PSt) with two polar, oil-resistant elastomers, i.e., chlorohydrin rubber (CHR) and chlorosulfonated polyethylene (CSPE), using the ionomer as compatibilizer were studied. The blends of the ionomer with polypropylene or high density polyethylene showed synergistic effects with respect to tensile strength. With increasing PSt content, the blends change their behavior from thermoplastic elastomer to toughened plastics. The synergism is probably because of the thermoplastic interpenetrating polymer networks formed in the blend. The blends exhibited high resistance against diesel oil or toluene.

When PSt was blended with CHR or CSPE using the ionomer as compatibilizer, only 2 or 3% ionomer was needed to enhance the mechanical properties of the blends. The effect is due to the ion–polar interaction of the ionomer with the polar polymer. The enhanced compatibility of the blends by the ionomer was demonstrated by DSC and Scanning electron micrograph. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1887–1894, 2006

Key words: blend; compatibilizer; styrene–butadiene–styrene triblock copolymer; ionomer; thermoplastic interpenetrating polymer network

INTRODUCTION

Recently, elastomers that contain ionic clusters or ionic domains as physical crosslinks have become of greater interest. Besides their attractive properties, they also produce some interesting blends with certain polymers. MacKnight and Lundberg¹ indicated in their review that sulfonated rubber ionomers can be used as a thermoplastic elastomer. Makowski et al.² prepared ethylene–propylene–diene (EPDM) ionomers by sulfonating it in hexane using acetyl sulfate, followed by neutralization with zinc acetate. Makowski and Lundberg³ denoted that it is necessary to use zinc stearate as an ionic plasticizer during processing of sulfonated EPDM ionomer. Canter⁴ obtained butyl rubber ionomer by sulfonation with SO₃–triethyl phosphate complex, followed by neutralization with NaOH, and studied their mechanical properties. Weiss et al.⁵ and

Storey et al.⁶ prepared hydrogenated styrene–butadiene–styrene triblock copolymer (SEBS) ionomer and styrene–isobutylene–styrene triblock copolymer ionomer by sulfonating them in 1,2-dichloroethane using acetyl sulfate, followed by neutralization with metallic acetate or alkali hydroxide, respectively.

However, the aforementioned ionomers were derived from rubbers with a low degree of unsaturation. Fitzgerald and Weiss,⁷ in their review, pointed out that rubbers with a high degree of unsaturation, such as polybutadiene or polyisoprene, cannot be sulfonated in 2–3% solution, since they gel easily during sulfonation. Later, Xie et al.⁸ found that in the presence of methyl ethyl ketone, styrene–butadiene rubber, which was obtained by emulsion polymerization of styrene and butadiene, can be sulfonated in petroleum ether using sulfuric acid and acetic anhydride as sulfonating agent, without gel formation. Recently, Xie et al.⁹ prepared sulfonated styrene–butadiene–styrene triblock copolymer (SBS) ionomer, using a similar method

Besides the attractive properties of the ionomers, they also produce some interesting blends with certain polymers. Gergen¹⁰ described the synthesis and prop-

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erties of some thermoplastic interpenetrating polymer networks (IPNs) based on SEBS and nylon-11 or polypropylene (PP). Siegfried et al.¹¹ described a series of thermoplastic IPNs based on SEBS and poly(styrene-isoprene-sodium methacrylate) ionomers. Sperling,¹² in his review, indicated that the blends of polymers containing glassy domains, ionic domains, and crystalline domains can form thermoplastic IPNs. Paul¹³ pointed out the synergism in strength in the polymer blends. In 1989, Xie et al. reported that the blends of sulfonated EPDM ionomer¹⁴ or sulfonated butyl rubber ionomer¹⁵ with crystalline PP, high-density polyethylene (HDPE), or SBS exhibited synergistic behavior with respect to tensile strength. Hara and Eisenberg¹⁶ indicated the miscibility enhancement via ion-dipole interaction between polystyrene (PSt) ionomer and poly(alkylene oxide).

This study deals with the blends of ionomer from sulfonated SBS with PP or HDPE, as well as its use as compatibilizer for PSt/chlorohydrin rubber (CHR) blends and for PSt/chlorosulfonated polyethylene(C-SPE) blends via the ion-dipole interaction.

EXPERIMENTAL

Materials

SBS YH801 with 30% styrene blocks and molecular weight of 1.1×10^5 is made by Yueyang Synthetic Rubber Factory. Chlorohydrin rubber (CHR) H-55 was supplied by Wuhan Synthetic Materials Factory. Polypropylene (PP) WH-T30S was supplied by Wuhan Petroleum Chemicals Co. High density polyethylene (HDPE) DGDA 6098 was purchased from Jilu Petroleum Chemicals Co. PSt 678U was purchased from Beijing YeShan Petroleum Chemicals Co. Acetic anhydride, sulfuric acid, zinc stearate, metallic acetates, ethyl alcohol, cyclohexane, and acetone were all chemically pure and used as received.

Sulfonation of SBS and neutralization of sulfonated sbs to form ionomers⁹

SBS ionomer was made through sulfonation of SBS in cyclohexane containing a small amount of acetone, using acetyl sulfate as the sulfonating agent made from sulfuric acid and acetic anhydride. SBS (100 g) was dissolved in a mixed solvent of 900 mL cyclohexane and 100 mL acetone, with stirring at room temperature. A mixture of 5 mL or 8.5 g of concentrated sulfuric acid with acetic anhydride at a molar ratio of sulfuric acid to acetic anhydride of 1/1.5–2.0 was dropped in at 25°C for 10 min. The reaction was carried out at 25°C for 0.5–1 h. Aliquot of the sulfonation solution was taken out and terminated with ethyl alcohol containing 0.5% (w/v) antioxidant 264 (2,6-ditert-butyl-4-methylphenol). The sample was pu-

rified by precipitating in ethyl alcohol and redissolving in cyclohexane/acetone three times before determining the sulfonate content of the product. The content of sulfonate groups, in milliequivalents (meq)/100 g sulfonated SBS, was measured by titration of a weighed amount of sulfonated sample (*W*) with an alcoholic solution of KOH using phenolphthalein as indicator. The sulfonate groups content or sulfonation degree was calculated as follows:

$$\text{Sulfonate groups content (\%)} = 100 \times N_{\text{KOH}} (V_1 - V_0) / W$$

where V_1 and V_0 represent the volume of alcoholic KOH solution used in the determination of the sample and the blank, respectively. N represents the normality of the alcoholic KOH solution.

Most portion of the sulfonated product was used to prepare ionomer. The sulfonation solution was neutralized by adding sodium hydroxide in an ethyl alcohol/water mixture at a neutralization degree of 1.2 equivalent ratio of NaOH/SO₃H, with stirring at room temperature for 1 h. The solvent was removed by flashing in hot water and the ionomer was dried.

Characterization

IR spectrum of the sodium sulfonated SBS ionomer (NaSSBS) was taken with a Bruker Equinox 55 FTIR spectrophotometer, using a KBr disc coated with a solution of the sample, followed by evaporation of solvent. DSC curves of the blends with or without NaSSBS as compatibilizer were taken using a Perkin-Elmer differential scanning calorimeter, with a heating rate of 20°C/min. Scanning electron micrograph (SEM) of broken section of the blend specimen with or without sulfonated SBS ionomer as compatibilizer was obtained by a JSM5610 scanning electron microscope.

Blending of the ionomer with polyolefin or of PSt with oil-resistant rubber in the presence of ionomer as compatibilizer

The NaSSBS was mixed with 10% zinc stearate, 1% antioxidant 264, and various proportions of HDPE or PP on a hot mill at 170 or 190°C for 15 min and compression molded at the same temperature under 10–15 MPa.

Blending of PSt with chlorohydrin rubber or chlorosulfonated polyethylene in different proportions with or without a small amount of the ionomer was carried out on a hot mill at 150 or 160°C, respectively, for 15 min, followed by compression molding at 150 and 160°C under 10–15 MPa, respectively.

TABLE I
Mechanical Properties of SBS Ionomer^a/PP Blends with Different Compositions in the Presence of 10% Zinc Stearate Based on the Ionomer

PP (wt %)	PP (vol %)	TS (MPa)	UE (%)	PS (%)
100	100	37.2	14	4
75	75.8	33.1	170	12
50	51.1	28.9	235	16
25	25.8	24.2	370	20
0	0	17.2	825	24
0 ^b	0	14.1	785	24

TS, tensile strength; UE, ultimate elongation; PS, permanent set.

^a Ionomer with sulfonation degree of 29.1 meq/100 g.

^b In the absence of zinc stearate.

Mechanical properties testing

Tensile strength and ultimate elongation of the blend were measured on a XL-2500 tensile tester, with a stretching rate of 250 mm/min. Permanent set was measured as percentage elongation 3 min after the specimen was broken and reunited.

RESULTS AND DISCUSSION

Characterization of NaSSBS with IR spectrum

The NaSSBS was characterized by IR spectrum, which showed the absorption peaks at 1042, 1180, and 1215 cm^{-1} because of the vibration of the sulfonate group. The absorption peak at about 800 cm^{-1} indicated the existence of disubstituted phenyl groups, which implies that the sulfonation occurs not only at polybutadiene segments, but also at the PSt segments.⁹ The characteristic absorption peaks at 960, 1640, and 3000 cm^{-1} were for the double bonds of polybutadiene units and those at 905 and 700, 750 and 905 cm^{-1} were for the phenyl rings of PSt units.

Blends of NaSSBS with polypropylene

It was found to be better to use zinc stearate as ionic plasticizer for the SBS ionomer, since it can lower the melt viscosity and improve the mechanical properties of the ionomer, as shown in Table I. Thus, the blending of PP or HDPE with the ionomer was also carried out in the presence of zinc stearate. Table I also lists the mechanical properties of the NaSSBS/PP blends with different compositions. With increasing PP, the blend changes its behavior from thermoplastic elastomer to toughened plastic. Figure 1 shows the relationship between tensile strength and vol % of PP in the blends. The straight line represents the theoretical linear additive relationship between tensile strength and composition of the blends. Obviously, a synergism was observed for tensile strength of the iono-

mer/PP blends, i.e., the tensile strength is higher than the calculated sum of tensile strength contributed by the two components. This may be attributed to the thermoplastic IPN formed in the blend, because both the ionic domains and the glassy domains in the SBS ionomer and also the crystalline regions or crystallites of the PP can be considered as physical crosslinks. Since there are some similarities between the methyl groups-containing amorphous phase of PP and the vinyl groups-containing polybutadiene block of SBS phase, the components show certain affinity for each other and the segments of different macromolecules diffuse into each other during melt blending, especially at interfaces between the two phases.¹⁵ At the interfaces, the two physical crosslinks penetrate into each other. This will enhance compatibility of the two components; thus, increasing the interfacial adhesion and the ability to transfer stress through the phases, resulting in synergism in strength.

Blends of NaSSBS with HDPE

Blending of the SBS ionomer with HDPE also proceeded more smoothly in the presence of 10% zinc stearate, based on the ionomer, than in the absence of it. Mechanical properties of the blends at different ratios of the components are shown in Table II. With increasing ratio of HDPE/ionomer, the blends change their behavior from thermoplastic elastomer to toughened plastic. Blends of the HDPE/ionomer also exhibit a synergistic effect between tensile strength and

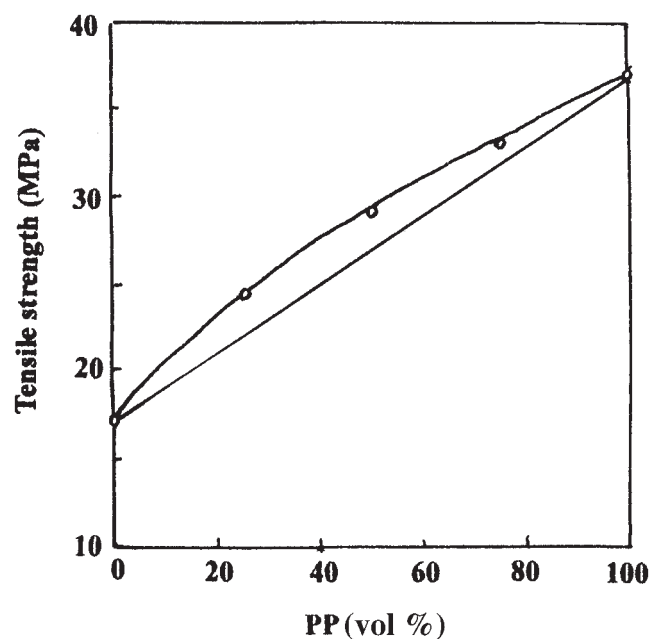


Figure 1 The relationship between tensile strength and composition (vol %) of the NaSSBS/PP blends.

TABLE II
Mechanical Properties of NaSSBS Ionomer^a/HDPE Blends with Different Compositions in the Presence of 10% Zinc Stearate Based on the Ionomer

HDPE (wt %)	HDPE (vol %)	TS (MPa)	UE (%)	PS (%)
100	100	29.2	46	4
75	74.7	27.6	126	12
50	49.6	24.1	210	20
25	24.7	19.6	340	16
0 ^b	0	17.2	825	24

TS, tensile strength; UE, ultimate elongation; PS, permanent set.

^a Ionomer with sulfonation degree of 29.1 meq/100 g.

^b In the absence of zinc stearate.

vol % of HDPE in the blends, except the blend containing 24.7 vol % HDPE, as shown in Figure 2.

HDPE is also a semicrystalline polymer like PP, containing both crystalline and amorphous regions. The crystalline regions or crystallites play the role of physical crosslinks. The blends of HDPE and SBS ionomer are also thermoplastic IPNs, because HDPE contains physical crosslinks from crystalline regions and SBS ionomer has physical crosslinks from both ionic domains and glassy PSt domains. The blends show the synergism with respect to tensile strength, probably because of the enhanced compatibility caused by the physical interpenetrating networks.

Oil or solvent absorbency of the blends of NaSSBS/PP or HDPE

Table III shows the resistance of the NaSSBS/PP and HDPE blends with different compositions against die-

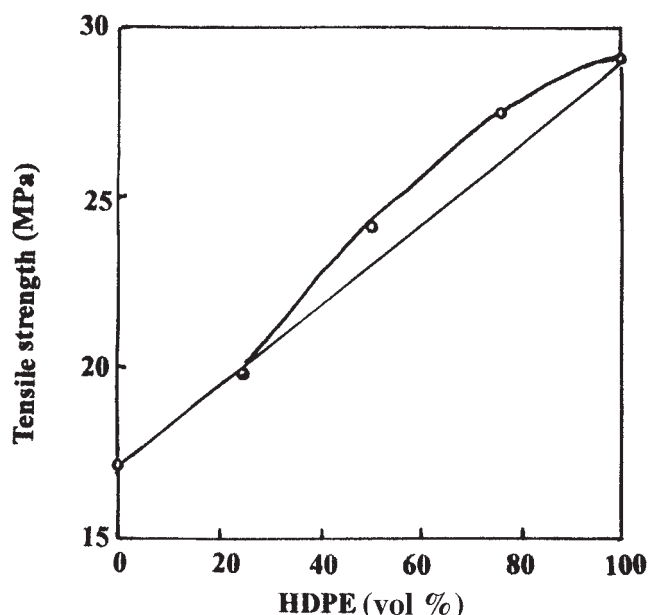


Figure 2 The relationship between tensile strength and composition (vol %) of the NaSSBS/HDPE blends.

TABLE III
Oil and Solvent Absorbency of the NaSSBS/PP and NaSSBS/HDPE Blends

NaSSBS/HDPE (wt ratio)	NaSSBS/PP (wt ratio)	Diesel oil absorbency (%)	Toluene absorbency (%)
100/0		Dissolved	Dissolved
75/25		38	47
50/50		13	27
25/75		9	11
	75/25	40	52
	50/50	15	38
	25/75	10	19

sel oil or toluene. When the sample of ionomer was immersed in diesel oil or toluene at room temperature for 48 h, it swelled and then dissolved. But its blends with PP or HDPE only absorbed a small amount of oil or toluene. The absorbency decreased with increasing polyolefin content. This fact also demonstrates the presence of thermoplastic interpenetrating networks in the blends or occlusion of some NaSSBS.

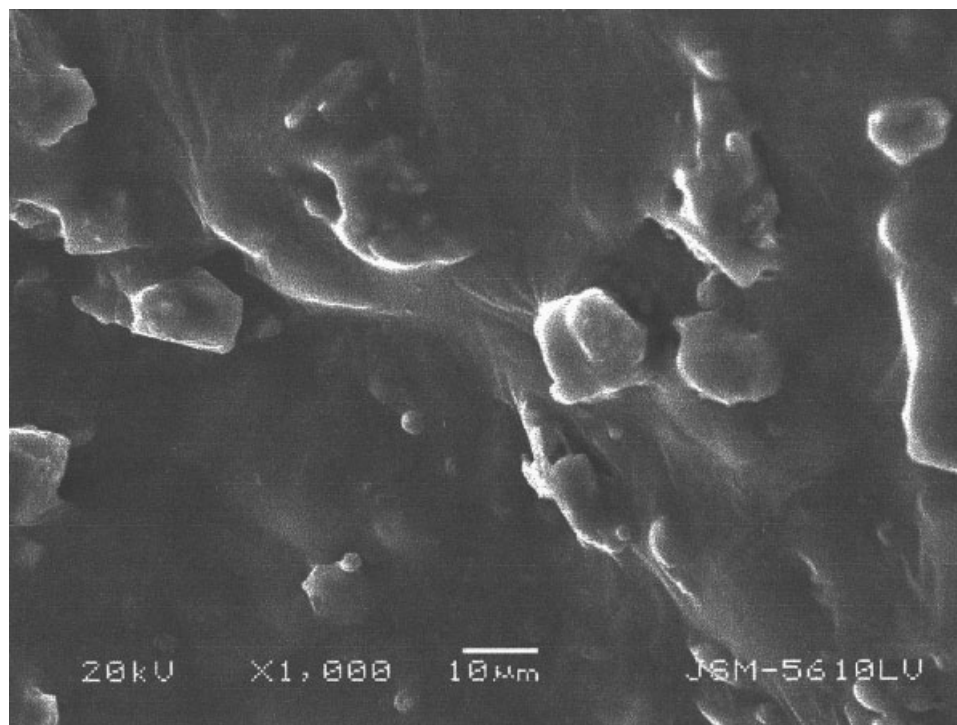
Blending of PSt with CHR, using NaSSBS as compatibilizer

The NaSSBS can be used as a compatibilizer for the blending of PSt with CHR, which is a polar, oil resistant, and vulcanizable elastomer. When PSt was blended with CHR alone in a weight proportion of 40/60, the tensile strength and ultimate elongation of the blend were low. But if a small amount of the ionomer is added to the blend, the mechanical properties improved; in particular, when the ionomer added reached 3 wt % of the blend, the tensile strength and the ultimate strength of the blend increased about 1.5 times, as shown in Table IV. However, the permanent set remained below 15%. The improvement of mechanical properties of the blend by the small amount of ionomer may be attributed to the improved interfacial adhesion via the ionomer, because on the one side the PSt block of the ionomer is miscible with

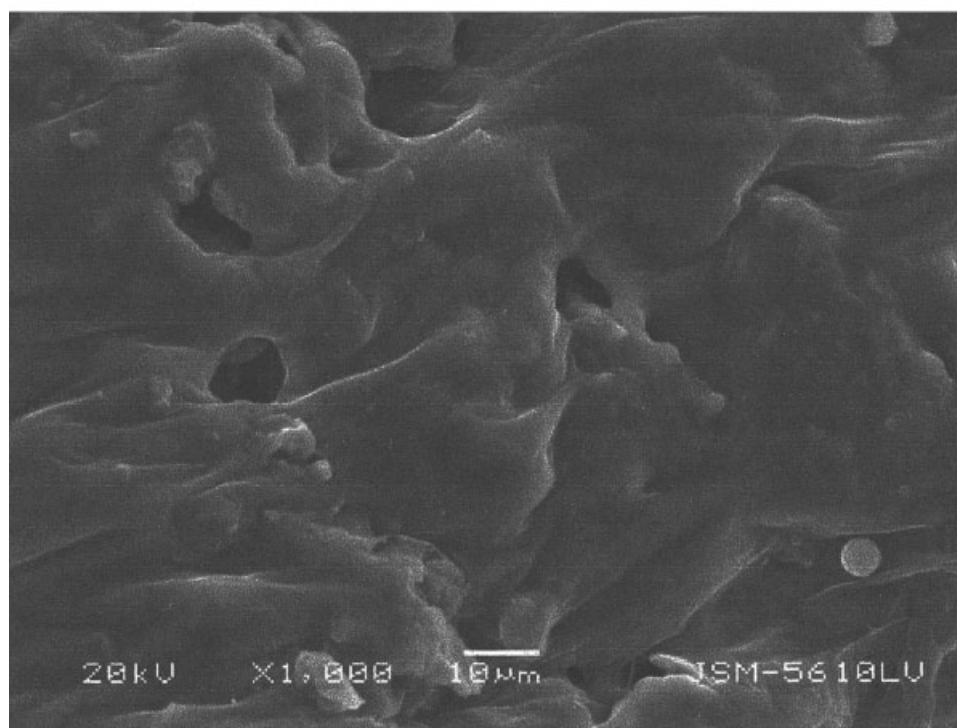
TABLE IV
Effect of the Amount of NaSSBS Ionomer used as Compatibilizer on the Mechanical Properties of PSt/CHR (40/60) Blends

Compatibilizer (wt %)	TS (MPa)	UE (%)	PS (%)
0	8.2	420	18
1	9.6	610	10
2	12.6	650	14
3	14.4	620	16
4	10.3	680	8
5	9.5	600	8

TS, tensile strength; UE, ultimate elongation; PS, permanent set.



(a)



(b)

Figure 3 The SEM micrographs of PSt/CHR blends with the ionomer (b) or without the ionomer (a) as compatibilizer (with magnification of 1000).

the PSt phase and on the other side there exists an ion-dipole interaction between ether linkages of CHR and the ionic groups of the ionomer. However, if the

ionomer was used at more than 4 wt % of the blend, the tensile strength of the blend decreased. This is probably because the ionic groups of the ionomer at

TABLE V
Effect of Composition on the Mechanical Properties of the PSt/CHR Blends in the Presence of 3 wt % of NaSSBS Ionomer

PSt/CHR (wt ratio)	TS (MPa)	UE (%)	PS (%)
0/100	4.2	1180	86
20/80	8.1	1010	16
40/60	14.4	620	28
50/50	35.9	380	20
60/40	49.2	66	14
80/20	69.5	7	2

TS, tensile strength; UE, ultimate elongation; PS, permanent set.

the surface of the PSt phase were shielded by the ionic groups of the excess ionomer used.

The enhanced compatibility of the two components by the ionomer can be demonstrated using DSC. The DSC curve of the blends without the addition of ionomer showed two T_g 's at -28.2 and 112.4°C , whereas that of the blends with the addition of 3% SBS ionomer showed two T_g 's at -4.4 and 113.9°C . The difference between the two T_g 's of the blend without the ionomer is 140.6°C , whereas the difference of the blend with the ionomer is 118.3°C . This indicates that the difference between T_g 's of the blend containing the ionomer becomes smaller than that without the ionomer. The inward shifting of T_g 's implies the enhanced compatibility of the two components of the blend. However, the T_g of PSt increased a little, which is probably due to the interaction of $-\text{SO}_3\text{Na}$ on the phenyl groups of SBS ionomer with $-\text{CH}_2\text{Cl}$ groups of CHR.

SEMs of the surface of broken section of the blend of PSt/CHR with or without addition of the ionomer as compatibilizer are shown in Figure 3. The surface of the broken section of the blend containing the ionomer seems to be smoother than that without the ionomer. Thus, it implies that the ionomer improves the interfacial adhesion between the surfaces of the two phases.

Table V shows that with increasing weight ratio of PSt/CHR, the tensile strength of the blend increases, whereas the ultimate elongation decreases. The blend changes its behavior from thermoplastic elastomer to toughened plastics. The blend with weight ratio of about 50/50 behaves as a strong thermoplastic elastomer with tensile strength of about 36 MPa, ultimate elongation of 380%, and permanent set of 20%.

Blending of PSt with chlorosulfonated polyethylene, using NaSSBS as compatibilizer

The sulfonated SBS ionomer can also enhance the compatibility between PSt and CSPE, which is an oil-resistant elastomer. When the two components were blended at a weight ratio of PSt/CSPE of 40/60 without addition of the ionomer, the tensile strength of the

TABLE VI
Effect of the Amount of Magnesium Sulfonated SBS Ionomer^a Added on the Mechanical Properties of PSt/CSPE (40/60) Blends

Compatibilizer/blend (wt %)	TS (MPa)	UE (%)	PS (%)
0	8.7	1050	100
1	10.3	960	80
2	13.9	1020	140
3	10.1	1220	120
4	9.6	890	85
5	9.0	920	90

^aSulfonation degree = 29.1 meq/100 g.

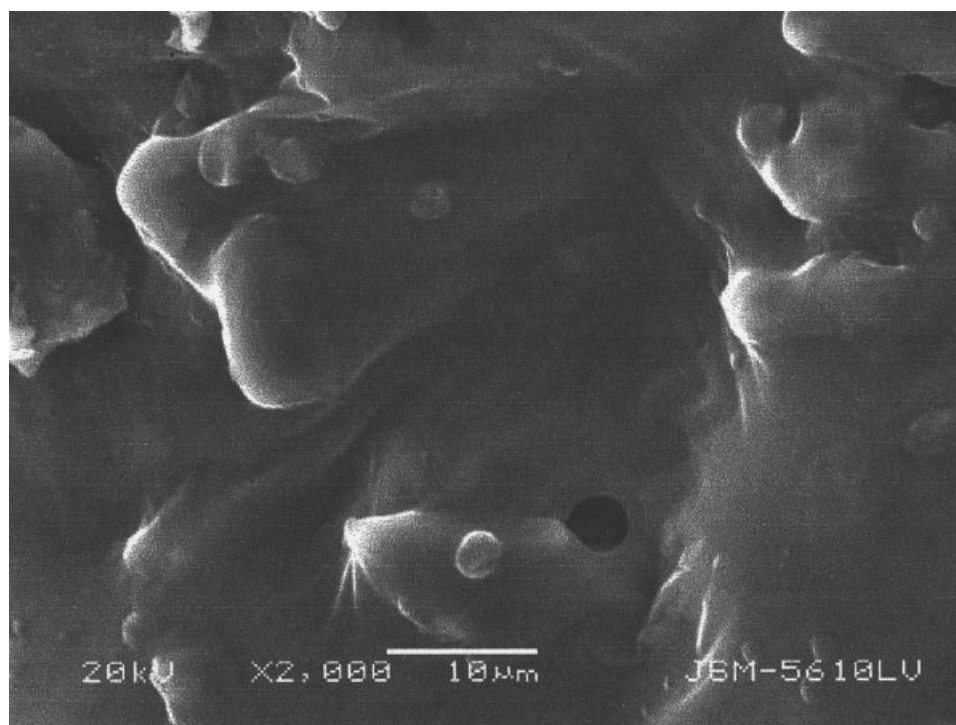
blend was low. However, when a small amount of magnesium SBS ionomer is added to the blend, the tensile strength increases, as shown in Table VI. With increase of the ionomer amount, the tensile strength of the blend increases to a maximum value at 2% ionomer, based on the blend. This phenomenon can be explained by the fact that the ionic groups of the ionomer can interact with the polar $-\text{SO}_2\text{Cl}$ groups of CSPE, whereas most of the PSt blocks of SBS ionomer can be compatible with the PSt phase, resulting in increasing interfacial adhesion and the compatibility of the two phases. However, excess ionomer added causes the tensile strength to diminish. This is probably because the ionic groups of the ionomer at the surface of PSt phase were shielded by the association of ionic groups of the excess SBS ionomer and cannot interact with the polar $-\text{SO}_2\text{Cl}$ groups of CSPE.

For a fixed amount of ionic compatibilizer, the tensile strength of the blends increases with increasing weight ratio of PSt/CSPE, whereas the ultimate elongation decreases, as shown in Table VII. This indicates that with increasing PSt component, the behavior of the blend changes from thermoplastic elastomer to the toughened plastic.

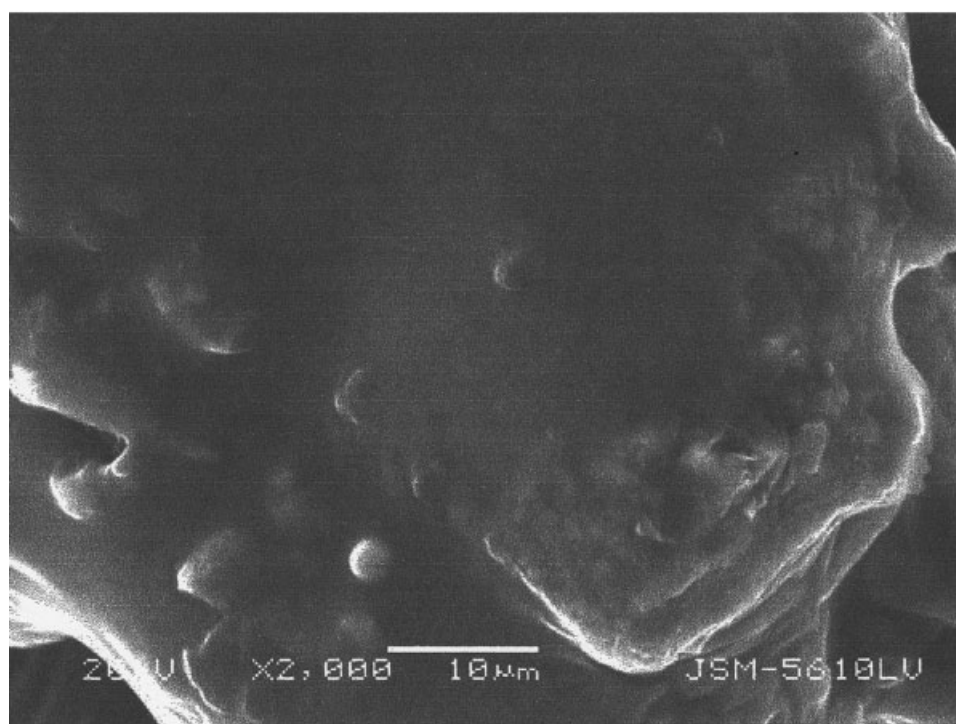
SEM in Figure 4 illustrate the surfaces of the broken section of the PSt/CSPE blends with or without addition of the ionomer as compatibilizer. The surface of the broken section of the blend with the addition of ionomer seems to be smoother than that without the

TABLE VII
Effect of Composition of PSt/CSPE Blend on Mechanical Properties of the Blends in the Presence of 3% Magnesium Sulfonated SBS Ionomer

PSt/CSPE (wt %)	TS (MPa)	UE (%)	PS (%)
0/100	4.5	2600	180
20/80	7.8	1670	180
40/60	10.1	1220	120
50/50	19.9	625	55
60/40	27.4	79	14
80/20	38.7	10	2



(a)



(b)

Figure 4 The SEM micrographs of PSt/CSPE blends with the ionomer (b) or without the ionomer (a) as compatibilizer (with magnification of 2000).

ionomer. This may probably be due to the improved adhesion between the surfaces of the two phases via the compatibilizer.

CONCLUSIONS

The blends of the sulfonated SBS ionomer with PP or HDPE showed synergistic effect with respect to tensile strength. With decreasing elastomeric ionomer content, the blends change their behavior from thermoplastic elastomer to toughened plastic. The synergism is probably because of the thermoplastic IPNs formed at interfaces of phases in the blend, which enhance the compatibility of the two components. The blends exhibited high resistance against diesel oil or toluene. When PSt was blended with CHR or CSPE, using the ionomer as compatibilizer, only 2 or 3% ionomer was needed to enhance the mechanical properties of the blends obviously. This fact is probably due to the ion-polar interaction of ionic groups of the SBS ionomer with the polar groups of the polar polymer, on the one hand, and due to the miscibility of the SBS part of the ionomer with the SBS phase, on the other hand. The enhanced compatibility of the blends by the ionomer was demonstrated by DSC and SEM.

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