

# Synthesis and Properties of Novel Amphiphilic Sulfated Ionomers by the Ring-Opening Reaction of an Epoxidized Styrene–Butadiene–Styrene Triblock Copolymer

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**ABSTRACT:** A method for the synthesis of novel sulfated ionomer of styrene–butadiene–styrene triblock copolymer (SBS) was developed. SBS was first epoxidized by performic acid in the presence of a phase-transfer catalyst; this was followed by a ring-opening reaction with an aqueous solution of alkali salt of bisulfate. The optimum conditions for the ring-opening reaction of the epoxidized SBS with an aqueous solution of  $\text{KHSO}_4$  were studied. During the ring-opening reaction, both phase-transfer catalyst and ring-opening catalyst were necessary to enhance the conversion of epoxy groups to ionic groups. The products were characterized with Fourier transform infrared spectrophotometry and transmission electron microscopy (TEM). After the potassium ions of the ionomer were substituted with lead ions, the lead sulfated ionomer exhibited dark spots under TEM. Some properties of the sulfated ionomer were studied. With increasing ionic groups or ionic potential of the cations, the water absorbency and emulsifying volume of the ionomer and the intrinsic vis-

cosity of the ionomer solution increased, whereas the oil absorbency decreased. The sulfated ionomer possessed excellent emulsifying properties compared with the sulfonated SBS ionomer. The sodium sulfated ionomers in the presence of 10% zinc stearate showed better mechanical properties than the original SBS. When the ionomer was blended with crystalline polypropylene, a synergistic effect occurred with respect to the tensile strength. The ionomer behaved as a compatibilizer for blending equal amounts of SBS and oil-resistant chlorohydrin rubber. In the presence of 3% ionomer, the blend exhibited much better mechanical properties and solvent resistance than the blend without the ionomer. SEM photographs indicated improved compatibility between the two components of the blend in the presence of the ionomer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2681–2688, 2008

**Key words:** blends; block copolymers; elastomers; ionomers; synthesis

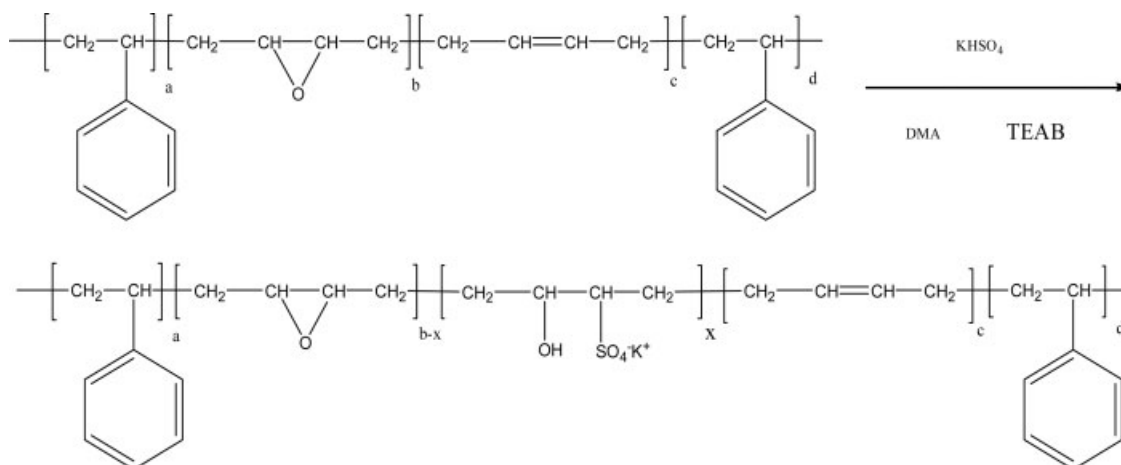
## INTRODUCTION

Ionomers of ethylene–propylene–diene copolymer (EPDM) or butyl rubber can be prepared by sulfonation in solution with acetyl sulfate and behave as thermoplastic elastomers in the presence of an ionic plasticizer.<sup>1–5</sup> Xie and Xu<sup>6</sup> pointed out that it is not necessary to use zinc stearate during the processing of alkylamine neutralized ionomers of sulfonated butyl rubber. However, Fitzgerald and Weiss<sup>7</sup> pointed out that rubber with a higher unsaturation degree cannot be sulfonated in solution at concentrations over 3% so as to avoid gelation. Styrene–butadiene–styrene triblock copolymer (SBS) with about 30–40% polystyrene block content is a thermoplastic elastomer with a higher

unsaturation degree. Samuel et al.<sup>8</sup> reported the sulfonation of styrene–butadiene rubber with a higher styrene content to obtain ionomers. Xie and coworkers<sup>9,10</sup> reported that in the presence of a small amount of ketone, both common styrene–butadiene rubber and SBS could be sulfonated in petroleum ether or cyclohexane without gelation. Nandi et al.<sup>11</sup> reported the preparation of sulfonated *cis*-1,4-polybutadiene ionomer via the reaction of *cis*-1,4-polybutadiene by  $\text{NaHSO}_3$  and benzoyl peroxide in the presence of a phase-transfer catalyst and oxygen. Udipi<sup>12</sup> epoxidized SBS by peracid in solution. The addition of nucleophilic reagents, such as acid, amine, and alcohol, to epoxidized polydiene was performed by Soutif et al.,<sup>13</sup> Jayawardena et al.<sup>14</sup> and Derouet et al.,<sup>15</sup> respectively. Soutif et al.<sup>13</sup> added naphthylacetic acid to epoxidized 1,4-polyisoprene with tetramethyl ammonium salt of the acid as a catalyst and obtained about 40% conversion at 100°C for 48 h. Derouet et al.<sup>15</sup> modified epoxidized 1,4-polyisoprene via a ring-opening reaction with alcohol with cerium ammonium nitrate as a catalyst. Recently, Xie

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Scheme 1

and coworkers<sup>16–18</sup> synthesized quaternary ammonium ionomer, sulfonated ionomer, and maleated ionomer of SBS by a ring-opening reaction of epoxidized SBS with triethylamine hydrochloride, NaHSO<sub>3</sub>, and potassium hydrogen maleate, respectively.

Recently, Antony and De<sup>19</sup> reviewed ionic thermoplastic elastomers. Although sulfonated ionomers of different rubbers have been studied, the sulfated ionomer has not yet been obtained. Su et al.<sup>20</sup> studied the mechanical properties of blends based on sulfated EPDM ionomer and polypropylene (PP). However, this kind of sulfated EPDM ionomer was really a sulfonated EPDM ionomer rather than a sulfated EPDM ionomer, because it was prepared by a mixture of acetyl anhydride and sulfuric acid, which was the same reagent used to obtain sulfonated EPDM.

This article deals with the synthesis conditions for the preparation of sulfated SBS ionomers, not sulfonated ionomers, via a ring-opening reaction of epoxidized SBS with an aqueous alkali salt of bisulfate solution. Characterization of the ionomers was carried out with Fourier transform infrared (FTIR) spectrophotometry and transmission electron microscopy (TEM). Their oil and water absorbencies, emulsifying properties, dilute solution properties, and mechanical properties, as well as blends with PP and their use as compatibilizers for blending SBS and oil-resistant chlorohydrin rubber (CHR), were studied to obtain a polar functionalized SBS with increasing interest for many applications, such as adhesives for polar substances, emulsifiers, and compatibilizers for blends of polar and nonpolar substances.

## EXPERIMENTAL

### Materials

SBS (YH791 type) was a product made by Yue-Yang Synthetic Rubber Factory (Yue-Yang, China) with a molecular weight of about 100 kg/mol and a polystyrene block content of 30 wt %. PP was supplied by

Ba-Lin Petroleum Chemicals Co. (Yue-Yang, China) Alkali salts of bisulfate were obtained by the reaction of sulfuric acid with alkali hydroxide at an equivalent ratio of 1 : 1. Lead acetates, acetone, formic acid (85%), hydrogen peroxide (30%), cyclohexane, toluene, poly(ethylene glycol) 600, tetraethyl ammonium bromide (TEAB), *N,N*-dimethyl aniline (DMA), and ethanol were chemically pure. Antioxidant 264 (2,6-di-*tert*-butyl-4-methylphenol) was an industrial product. Hydrochloric acid (36%) and KOH were analytical reagents.

### Epoxidation of SBS in the presence of a phase-transfer catalyst

Epoxidation of SBS was carried out via the reaction of SBS in a cyclohexane solution (SBS concentration = 11 g/100 mL) with performic acid formed from 85% HCOOH and a 30% aqueous H<sub>2</sub>O<sub>2</sub> solution *in situ* at 70°C for 4 h with 1 wt % poly(ethylene glycol) 600/SBS as a phase-transfer catalyst. The molar ratio of H<sub>2</sub>O<sub>2</sub>/HCOOH was 1. The epoxidized SBS (ESBS) was precipitated and washed several times with 95% ethanol until it was neutral; then, it was dried in a vacuum dryer at 60°C.

### Ring-opening reaction of ESBS with KHSO<sub>4</sub> to form the ionomer (Scheme 1)

ESBS was first dissolved in toluene to form a solution with a concentration of 12 g/100 mL, into which was added 5 wt % TEAB/ESBS as a phase-transfer catalyst and 5 wt % DMA/ESBS as a ring-opening catalyst. An aqueous solution of KHSO<sub>4</sub> was then added under vigorous stirring at 75°C for 7 h with a KHSO<sub>4</sub>/epoxy group molar ratio of 1.8. The reaction was terminated by the addition of an excess of KOH solution with stirring for 10 min to neutralize the unreacted KHSO<sub>4</sub>. The mixture was precipitated by 95% ethanol containing a small amount of antioxidant 264, and the salt powder precipitated simultaneously at the bottom was removed. The precipitated ionomer was redissolved in toluene and

again precipitated with 95% ethanol three times; the precipitate was then dried in a vacuum dryer at 60°C.

### Chemical analysis

Epoxy groups in the ESBS were determined by the HCl–acetone method<sup>21</sup> as follows. About 1 g of sample was accurately weighed into an iodometric titration flask. HCl–acetone (25 mL; 1/80 v/v) solution was added. The flask was stoppered, and the mixture was stirred until the sample was dissolved. After it stood in the dark for 1 h, three drops of phenolphthalein indicator were added, and the solution was titrated with a standard alcoholic KOH solution to a pink color.

$$\text{Epoxy value} = (V_0 - V_1)N/10W$$

where  $V_0$  and  $V_1$  represent the volumes (mL) of the standard alcoholic KOH solution used in titration for the blank and sample, respectively;  $W$  is the weight of the sample; and  $N$  is the normality of the alcoholic KOH solution.

The conversion of the epoxy groups to sulfate groups was obtained by the subtraction of two epoxy values determined before and after the ring-opening reaction divided by the original epoxy value.

### Characterization

The FTIR spectrum of the potassium sulfated SBS ionomer was recorded with a Bruker Equinox 55 FTIR spectrophotometer (Ettlingen, Germany) with a KBr disc coated with a solution of the sample, followed by the evaporation of the solvent. A transmission electron micrograph of the lead-ion-neutralized SBS ionomer was obtained with a JEM-100CXII transmission electron microscope (JEOL, Ltd., Japan) after the potassium ionomer was treated with lead acetate solution, washed with water, and dried. Scanning electron micrographs (JEOL, Ltd., Japan) were taken by a JSM-5610 electron microscope after the broken section of the blend sample was vacuum-deposited with golden vapor.

### Oil and water absorbencies of the ionomer

Oil absorbency and water absorbency were determined by immersion of an accurately weighed sample ( $W_b$ ) in kerosene oil or water at room temperature for 48 h, followed by the removal of the liquid on the surface of the sample with filter paper, and then, the weighing of the sample ( $W_a$ ).

$$\text{Absorbency (\%)} = (W_a - W_b) \times 100/W_b$$

### Solution viscosity of the ionomer

The intrinsic viscosity ( $[\eta]$ ) of the ionomers in chloroform was measured by an Ubbelohde viscometer at 25°C.

### Mechanical properties of the ionomer

The ionomer was mixed with a certain amount of zinc stearate on a hot roll and then hot-pressed at 160°C. Its tensile strength and ultimate elongation were measured on a XL-2500 tensile tester (Chang-Sha, China) at a stretching rate of 250 mm/min. Permanent set was measured as percentage elongation 3 min after the specimen was broken and reunited.

### Blending of the ionomer with polyolefin

The ionomer was mixed with 10% zinc stearate, 1% antioxidant 264, and a certain proportion of PP on a hot mill at 170 to 190°C within 15 min, depending on the amount of PP used. The blend was compression-molded at the same temperature under 10–15 MPa.

### Blending of SBS with CHR in the presence of the ionomer as a compatibilizer

Blending of SBS with CHR in a 1:1 weight proportion with or without a small amount of the ionomer was carried out on a hot mill at 160°C for 15 min, and the sample was compression-molded at 160°C under 10–15 MPa of pressure.

## RESULTS AND DISCUSSION

### Synthesis conditions for the sulfated SBS ionomer

Preliminary experiments showed that it was necessary to use a phase-transfer catalyst and a ring-opening catalyst in the ring-opening reaction of ESBS with  $\text{KHSO}_4$ , so as to obtain a high epoxy group conversion. The tests for various factors affecting the epoxy group conversion stated in the following text were carried out in the conditions described in the Experimental section.

Because the reaction was carried out in both the aqueous solution of  $\text{KHSO}_4$  and the toluene solution of ESBS, the ring-opening reaction of ESBS with  $\text{KHSO}_4$  to form the sulfated ionomer was difficult and could be accelerated by the addition of a phase-transfer catalyst. Table I shows the effect of TEAB as

TABLE I  
Effect of the Amounts of DMA and TEAB on the Epoxy Conversion of ESBS

DMA/ ESBS (wt %)	TEAB/ ESBS (wt %)	Epoxy conversion (%)
0	5	21.5
3	5	35.4
5	5	41.7
7	5	43.2
5	0	26.8
5	3	36.8
5	5	41.7
5	7	43.5

**TABLE II**  
Effect of the Amount of KHSO<sub>4</sub> and the ESBS Concentration on the Epoxy Conversion of ESBS

PBS/epoxy group (molar ratio)	ESBS concentration (g/100 mL)	Epoxy conversion (%)
1.6	12	30.8
1.8	12	41.7
2.0	12	35.4
1.8	10	29.6
1.8	12	41.7
1.8	14	Gel

a phase-transfer catalyst on the conversion of epoxy groups to potassium sulfate groups. The conversion of epoxy groups increased with increasing amount of TEAB. The optimum amount was 5 wt % TEAB based on ESBS, as the epoxy conversion increased slowly over 5 wt % TEAB.

DMA can be used as a catalyst for the ring-opening reaction of epoxy groups with carboxylic acid; thus, it was tested as a catalyst for the ring-opening reaction of epoxy groups of ESBS with KHSO<sub>4</sub> to form the sulfated ionomer of SBS. The addition of DMA could increase the epoxy conversion. Over 5 wt % DMA, the epoxy conversion increased slowly, as shown in Table I.

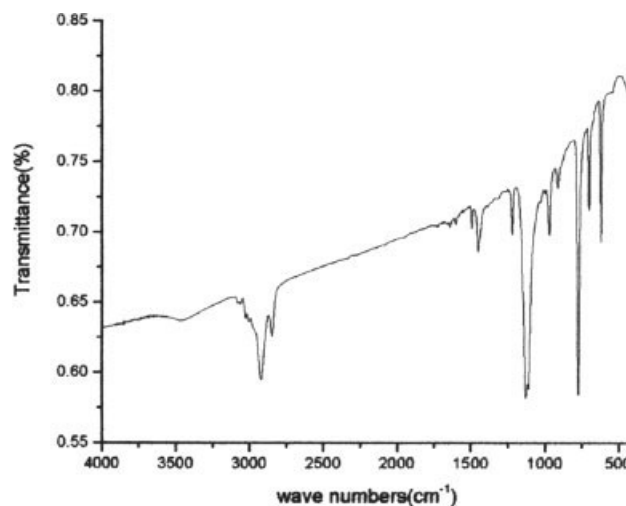
The effect of the molar ratio of KHSO<sub>4</sub>/epoxy groups on the conversion of the epoxy groups of ESBS is shown in Table II. The conversion increased with increasing molar ratio of the KHSO<sub>4</sub>/epoxy groups. The optimum molar ratio was 1.8 : 1, over which the conversion decreased gradually. An optimum molar ratio much higher than 1 : 1 was due to the heterogeneous reaction.

Table II also indicates that with increasing ESBS concentration, the conversion of epoxy groups into KSO<sub>4</sub><sup>-</sup> groups increased obviously from 10 to 12 g/100 mL. The epoxy conversion reached about 42% at an ESBS concentration of 12%. However, the reaction solution became too viscous and then formed gel when the ESBS concentration was over 14 g/100 mL. Hence, the optimum ESBR concentration was 12 g/100 mL.

Table III shows that the epoxy group conversion increased with reaction time rapidly before 7 h and

**TABLE III**  
Effects of the Reaction Temperature and Time on the Epoxy Conversion

Temperature (°C)	Time (h)	Epoxy conversion (%)
65	7	28.6
70	7	36.4
75	7	41.7
80	7	35.7
75	5	31.5
75	6	36.8
75	7	41.7
75	8	43.1



**Figure 1** FTIR spectrum of the sulfated SBS ionomer.

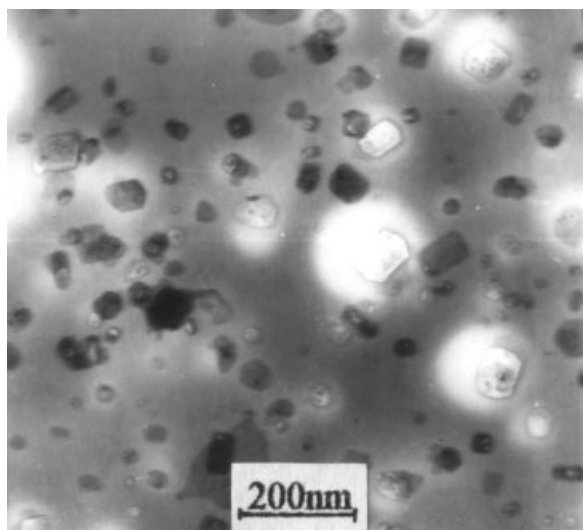
then gradually. To obtain a higher conversion of epoxy groups, a long reaction time seemed necessary.

Table III also shows the effect of the reaction temperature on the conversion of epoxy groups to sulfate groups. The reaction rate increased with temperatures below 75°C and then decreased, probably due to the side reactions at too high temperatures. The optimum temperature was 75°C.

### Characterization of the sulfated SBS ionomer

The FTIR spectrum of the KSO<sub>4</sub><sup>-</sup> groups containing SBS (Fig. 1) showed that there existed absorption peaks at 910, 968, and 730 cm<sup>-1</sup> for the double bonds of polybutadiene segments and at 699 and 1450 cm<sup>-1</sup> for the phenyl groups. A broad absorption peak at 3450 cm<sup>-1</sup> existed for OH groups, which was formed simultaneously during the ring-opening reaction of the epoxy groups with KHSO<sub>4</sub>. The absorption peaks at 810 and 880 cm<sup>-1</sup> were due to the unreacted epoxy groups. The existence of absorption peaks at 1219 and 1448 cm<sup>-1</sup> were attributed to the S=O of the sulfate groups in the main chains. Thus, the IR spectrum indicated the functional groups of the sulfated SBS ionomer.

A transmission electron microphotograph (Fig. 2) showed black spots in the specimen of the lead sulfated SBS ionomer, which was obtained by the exchange of the potassium sulfated SBS ionomer with lead acetate in solution for 24 h, followed by washing and drying. Because the lead ions could absorb the electrons and the ions associated into ionic domains, the latter appeared as dark spots under TEM. The shape of the dark spots exhibited somewhat cylindrical type with lengths in the range of 10<sup>1</sup> nm. Thus, TEM demonstrated that the product obtained was an ionomer, which also seemed to be a nanocomposite at a molecular level.



**Figure 2** TEM microphotograph of the lead sulfated SBS ionomer.

#### Some properties of the potassium sulfated SBS ionomer

The ionomer could absorb water because it contained hydrophilic ionic groups. Table IV indicates that with increasing ionic groups, the water absorbency increased, more obviously over 0.5 mmol of ionic groups/g. The water absorbency of the ionomer containing sulfate groups was much higher than that of the ionomer containing sulfonate groups, even up to seven times higher.<sup>17</sup>

Table IV also shows that the ionomer offered some kerosene-resistant properties. The oil absorbency of the ionomer decreased with increasing ionic groups. This fact was attributed to the association of the ionic groups in the nonpolar oil, resulting in oil resistance.

$[\eta]$  of the ionomers in chloroform increased with increasing ionic groups, as shown in Table IV. This phenomenon could be explained by the fact that the more the ionic groups there were, the more the association between the ionic groups of the ionomer macromolecules was, which resulted in higher resistance to flow or higher viscosity.

Table V denotes that with increasing ionic potential of the cations in the ionomer, the water absorbency and  $[\eta]$  of the ionomer increased, whereas the oil

**TABLE IV**  
Effect of the Ionic Group Content on the Oil Absorbency, Water Absorbency, and Dilute Solution Viscosity of the Ionomers

Ionic group content (mmol/g)	Water absorbency (%)	Kerosene absorbency (%)	$[\eta]$ (mL/g)
0.48	10.8	698	116
0.92	76.4	402	142
1.20	146	189	161
1.64	232	46.5	184

**TABLE V**  
Effects of Cations on the Water Absorbency, Oil Absorbency, and Dilute Solution Viscosity

Cation	Ionic potential	Ionic group content (mmol/g)	Water absorbency (%)	Kerosene absorbency (%)	$[\eta]$ (mL/g)
Li <sup>+</sup>	1.46	1.45	284	31.4	221
Na <sup>+</sup>	1.03	1.56	251	38.9	198
K <sup>+</sup>	0.75	1.64	232	46.5	184

absorbency decreased. The higher the ionic potential of the cation in the ionomer was, the higher the repulsive force between the sulfate groups in the macromolecule was and the more straight the macromolecules were; this resulted in the higher viscosity.

Because the ionomer contains both hydrophilic ionic groups and hydrophobic SBS segments, it exhibited amphiphilic properties and could emulsify the toluene and water system. Table VI shows that the emulsifying volume increases with increasing ionic groups used because of the increase in emulsifying centers. The ionomer possessed excellent emulsifying properties, as the emulsifying volume even reached over 95 mL when 0.2 g of the ionomer with 1.64 mmol/g of sulfate groups was used. The emulsifying properties of the ionomer containing sulfate groups was much better than that of the ionomer containing sulfonate groups. The emulsifying volume of the latter was only 36 mL at about 1.6 mmol/g of sulfonate groups.

The emulsifying volume also increased with increasing ionic potential of the cations, as indicated in Table VI.

#### Mechanical properties of the sodium sulfated SBS ionomer

It was better to process the sodium sulfated ionomer in the presence of zinc stearate to lower the melt viscosity. Table VII shows the tensile strength, ultimate elongation, and permanent set of the ionomer in the presence of various amounts of zinc stearate. The tensile strength and ultimate elongation increased

**TABLE VI**  
Effect of the Ionic Group Content on the Emulsifying Property of the Ionomer

Cation	Ionic potential	Ionic group content (mmol/g)	Ionomer content (g/100 mL)	Emulsifying volume (mL)
K <sup>+</sup>	0.75	0.48	0.2	31.5
K <sup>+</sup>	0.75	0.92	0.2	49.2
K <sup>+</sup>	0.75	1.20	0.2	76.4
K <sup>+</sup>	0.75	1.64	0.2	95.8
Li <sup>+</sup>	1.46	1.45	0.1	82.1
Na <sup>+</sup>	1.03	1.56	0.1	75.7
K <sup>+</sup>	0.75	1.64	0.1	68.6

**TABLE VII**  
Effect of the Amount of Zinc Stearate Added on the Mechanical Properties of the Sodium Sulfated SBS Ionomers

Zinc stearate/ionomer (%)	0	5	10
Tensile strength (MPa)	12.6	16.2	18.4
Ultimate elongation (%)	989	1070	1590
Permanent set (%)	11	18	26

The ionic group content of the ionomer was 1.17 mmol/g.

with increasing amounts of zinc stearate as an ionic plasticizer up to 10%. When the ionomer was mixed with 15% zinc stearate, excess zinc stearate separated out during melt mixing and during molding. The effect of zinc stearate on the mechanical properties of the ionomer could be interpreted as follows: with increasing amounts of zinc stearate, more zinc stearate was distributed in the ionic domains of the ionomer; this made the size of the domains diminish and the number of domains, or the number of physical crosslinks, increase, which resulted in an increase in tensile strength. Uniform distribution of ionic domains in the presence of zinc stearate also made the exchange of ionic bonds easier; this increased the ultimate elongation of the ionomer. However, excess zinc stearate separated out.

Table VIII indicates that with increasing sulfate ionic group content, both the tensile strength and ultimate elongation increased due to the increased number of ionic domains formed in the ionomers with higher sulfate contents. However, with increasing ionic groups exceeding 1.17 mmol/g, the tensile strength and ultimate elongation of the ionomer decreased. This fact was interpreted as the excess physical crosslinks formed by too many or too large ionic domains.

The mechanical properties of the sulfated SBS ionomer were better than those of maleated SBS ionomer.<sup>18</sup> This was attributed to the stronger association forces of the sulfate ions than that of the maleate ions.

#### Blends of the sodium sulfated SBS ionomer with PP

Table IX lists the mechanical properties of the sodium sulfated SBS ionomer/PP blends with different

**TABLE VIII**  
Effect of the Ionic Group Content on the Mechanical Properties of the Sodium Sulfated SBS Ionomer

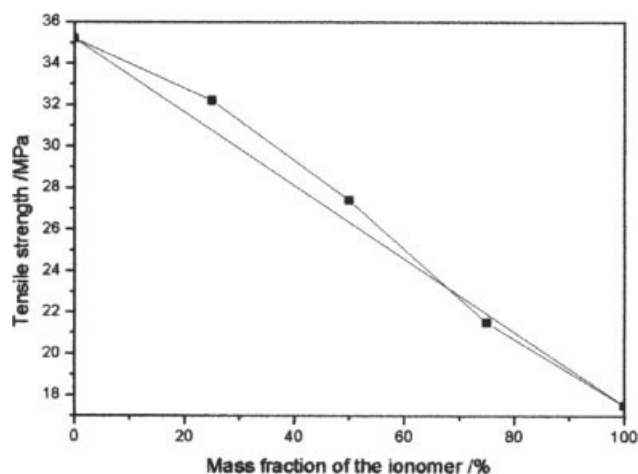
Ionic group content (mmol/g)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	9.14	420	16
0.45	13.8	860	18
0.89	16.5	1280	24
1.17	18.4	1590	26
1.60	14.6	1160	20

**TABLE IX**  
Effect of the Ionomer Content on the Mechanical Properties of the Ionomer/PP Blends

Ionomer/PP (weight ratio)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0/100	35.2	1.20	—
25/75	32.2	7.38	—
50/50	27.4	172	18
75/25	21.5	1010	24
100/0	17.5	1447	25

The ionic group content of the ionomer was 1.11 mmol/g.

compositions. With increasing PP, the blend changed its behavior from a thermoplastic elastomer to a toughened plastic. Figure 3 shows the relationship between the tensile strength and composition of the blends. The straight line represents the theoretical additive relationship between the tensile strength and the composition of the blends. Obviously, except for the blend containing 75% ionomer, a synergism was observed for the tensile strength of the ionomer/PP blends; that is, the tensile strength of the blend was higher than the calculated sum of the tensile strengths contributed by the two components. This was attributed to the thermoplastic interpenetrating polymer network 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 could be considered physical crosslinks. Because there were some similarities between the methyl-group-containing amorphous phase of PP and the vinyl-group-containing SBS phase, the components showed a certain affinity for each other, and during melting, the segments of different macromolecules diffused into each other at interfaces between the two phases, where the three physical crosslinks penetrated into each other and



**Figure 3** Relationship between the ionomer content and the tensile strength of the ionomer/PP blends.

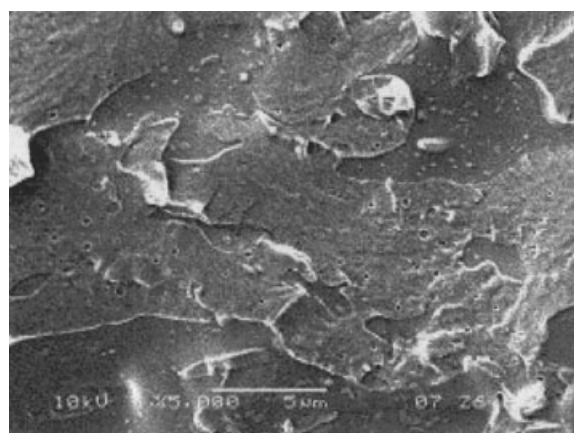
enhanced the compatibility of the two components; this increased the interfacial adhesion and the ability to transfer stress through phases, which resulted in synergism in strength.<sup>22</sup>

The blend with a weight ratio of PP/SBS of 1 : 1 showed a toluene absorbency of 4.8%, whereas SBS was soluble in toluene. This fact indicates that the two components became quite compatible because of the enhanced compatibilization by the thermoplastic interpenetrating network formed from the crystalline PP domains and the polystyrene glass domains and ionic domains in the blend.

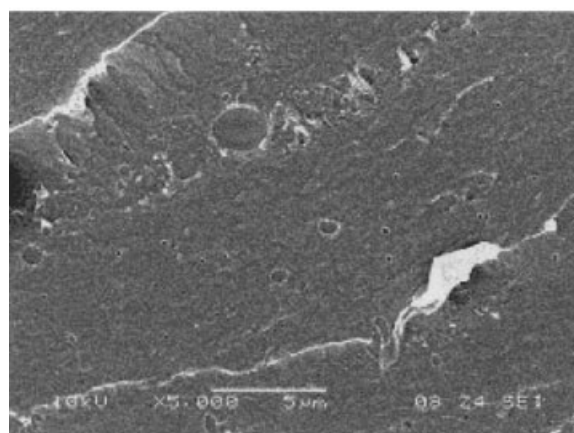
#### Blending of SBS with CHR with sodium sulfated SBS ionomer as a compatibilizer

According to the ion–dipole interaction, the sulfated SBS ionomer could be used as a compatibilizer for the blending of SBS with CHR, which was a polar, oil-resistant, and vulcanizable elastomer containing ether linkages. When a small amount of the ionomer was added to the blend of SBS and CHR in a weight proportion of 50:50, the mechanical properties of the blend were improved. Especially when the ionomer loading reached 3 wt % of the blend, both the tensile strength and the ultimate strength of the blend increased 1.7 times, as shown in Table X. However, the permanent set was kept at about 20%. Thus, the blends still behaved as thermoplastic elastomers. The improvement in the mechanical properties of the blend by a small amount of ionomer was attributed to the interfacial adhesion via the ionomer because, on the one hand, the SBS backbone of the ionomer was miscible with the SBS phase and on the other hand, there existed an ion–dipole interaction between the ether linkage 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 was probably because the ionic groups of the ionomer at the surface of the SBS phase were shielded by the ionic groups of the excess ionomer used.

The enhanced compatibility of the two components by the ionomer was demonstrated by SEM. SEM microphotographs of the surface of broken sec-



(a)



(b)

**Figure 4** SEM microphotographs of the SBS/CHR blends (a) without and (b) with 3% ionomer at a magnification of 5000 $\times$ .

tions of the SBS/CHR blend with or without the addition of the ionomer as a compatibilizer are shown in Figure 4. The surface of the broken section of the blend containing the ionomer was smoother than that without the ionomer. This implies that the ionomer improved the interfacial adhesion between the surfaces of the two phases.

The effect of the sulfated SBS ionomer as a compatibilizer was stronger than that of the maleated SBS ionomer. In the former case, 3% ionomer could raise both the tensile strength and ultimate elongation about 1.7 times, whereas in the latter case, 3% ionomer could only raise those mechanical properties 1.2 times.<sup>18</sup> This may have been due to the stronger ion–dipole interaction of the sulfate ion with the ether linkages of CHR than that of the maleate ion.

The SBS/CHR (1 : 1) blend without the ionomer as a compatibilizer absorbed about 90% kerosene, whereas that with the ionomer absorbed about 52% kerosene. This also indicates that the ionomer enhanced the compatibility of SBS and CHR in the blend, which exhibited a higher oil resistance.

**TABLE X**

**Effect of the Amount of the Sodium Sulfated Ionomer Added on the Mechanical Properties of the SBS/CHR Blends**

Iononer/ blend (weight %)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	8.64	856	16
1	11.8	987	17
2	13.5	1330	20
3	14.8	1520	23
4	13.7	1580	25
5	12.6	1500	24

## CONCLUSIONS

A novel method for the preparation of a sulfated ionomer of SBS was developed by a ring-opening reaction of epoxidized SBS with alkali bisulfate. During the ring-opening reaction of epoxidized SBS with  $\text{KHSO}_4$ , both a phase-transfer catalyst and ring-opening catalyst were necessary to enhance the conversion of epoxy groups to ionic groups. The optimum conditions were as follows: ESBS concentration, 120 g/L; molar ratio of  $\text{KHSO}_4$ /epoxy groups, 1.8; weight ratio of TEAB/ESBS, 5%; weight ratio of DMA/ESBR, 5%; and temperature, 75°C for 7 h. The FTIR spectrum of the potassium sulfated SBS ionomer demonstrated the characteristic groups of the ionomer. TEM of the lead sulfated ionomer demonstrated the presence of ionic domains as dark spots. With increasing ionic group content and ionic potential of the cation of the sulfated ionomer, the water absorbency and dilute solution viscosity increased, whereas its oil absorbency decreased. The emulsifying volume increased with increasing ionic groups, and ionic potential of cations in the ionomer. These properties demonstrated the amphiphilic nature of the ionomer. The sodium sulfated ionomer in the presence of 10% zinc stearate showed better mechanical properties than the original SBS. The tensile strength and ultimate elongation of the ionomer increased with increasing ionic group content up to 1.17 mmol/g of ionomer. When the ionomer was blended with PP, a synergistic effect occurred with respect to the strength, probably due to the thermoplastic interpenetrating network formed in the blend of the ionomer containing ionic and glass domains and PP-containing crystalline domains. The ionomer behaved as a compatibilizer for blending equal amounts of SBS and oil-resistant CHR through ion-dipole interactions. In the presence of 3% ionomer,

the blend exhibited much better mechanical properties and solvent resistance than the blend without the ionomer. The blends behaved as thermoplastic oil-resistant elastomers. SEM photographs indicated increased compatibility between the two components in the presence of the ionomer.

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