Synthesis, Characterization and Properties of Novel Amphiphilic Phosphated Ionomers by Ring-Opening Reaction of Epoxidized Styrene-Butadiene-Styrene Triblock Polymer

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A method for synthesis of novel phosphated ionomer of (styrene-butadiene-styrene) triblock polymer (SBS) from epoxidized SBS was developed. The optimum conditions for the ring-opening reaction of the epoxidized SBS with aqueous solution of disodium hydrogen phosphate were studied. It was found that during the ring-opening reaction phase transfer catalyst, ring-opening catalyst and pH regulator were necessary to enhance the conversion of epoxy groups to ionic groups. The products were characterized with Fourier Transform Infrared Spectrophotometry (FTIR) and transmission electron microscopy (TEM). Some properties of the phosphated ionomer were studied. With increasing ionic groups or the ionic potential of the cation of the ionomer, the water absorbency emulsifying volume and the intrinsic viscosity of the ionomer increase, whereas the oil absorbency decreases. The ionomer possesses excellent emulsifying property, as compared with the sulfonated ionomer. The disodium phosphated ionomers in the presence of 10% zinc stearate showed better mechanical properties than the original epoxy SBS. Optimum mechanical properties occurred at the ionic group content of 0.95 mmol/g ionomer. When the ionomer was blended with crystalline polypropylene, a synergistic effect occurs with respect to the tensile strength. The ionomer behaves as a compatibilizer for blending equal amount of SBS and oil-resistant chlorohydrin rubber (CHR) to form an oil resistant thermoplastic elastomer. SEM microphotographs indicated enhanced compatibility between the two components of the blend in the presence of the ionomer.

Keywords: ionomer; epoxidized rubber; ring-opening reaction; (styrene-butadiene-styrene) triblock copolymer; blend; compatibilizer

1 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 (1–3). Xie et al. reported the melt flow properties, solution behavior, dynamic mechanical properties and mechanical properties of sulfonated EPDM ionomers (4) and butyl rubber ionomers (5), both of which were obtained by sulfonation with acetyl sulfate in petroleum ether and neutralization with metallic acetates or alkylamines. It was pointed out that it is not necessary to use zinc stearate during processing of alkylamine neutralized ionomers of sulfonated butyl rubber (5). However, Fitzgerald

and Weiss (6) pointed out that the rubber with higher unsaturation degree cannot be sulfonated in solution in concentration 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 higher unsaturation degree. Samuel et al. (7) reported the sulfonation of styrene-butadiene rubber(SBR) with higher styrene content to obtain ionomers, which act as thermoplastic elastomer. Xie et al. (8, 9) reported that in the presence of small amount of ketone, both common SBR with 23% styrene content and SBS can be sulfonated in petroleum ether or cyclohexane without gelation. Nandi et al. (10) reported the preparation of sulfonated cis-1,4 polybutadiene ionomer via reaction of cis-1,4 polybutadiene by NaHSO₃ and benzoyl peroxide in the presence of a phase transfer catalyst and oxygen. Udipi (11) epoxidized SBS by peracid in solution. Addition of nucleophilic reagents, such as acid, amine and alcohol onto epoxidized polydiene were performed by Soutif et al. (12), Jayawardena et al. (13) and

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Derouet et al. (14), respectively. Soutif et al. (12) added naphthylacetic acid to epoxidized 1,4-polyisoprene using tetramethyl ammonium salt of the acid as catalyst, and obtained about 40% conversion at 100°C for 48 h. Derouet et al. (14) modified epoxidized 1,4-polyisoprene via ring-opening reaction with alcohol using cerium ammonium nitrate as catalyst. Recently, Xie et al. (15, 16) synthesized quaternary ammonium ionomer of SBS and sulfonated ionomer of SBR by ring-opening reaction of epoxidized SBS with triethylamine hydrochloride and by ring-opening reaction of epoxidized SBR with NaHSO$_3$, respectively.

Recently Antony and De (17) gave a review about ionic thermoplastic elastomers. Capek (18) discussed the effect of ionic functional groups in polymers on the formation of non-traditional polymer materials, polymer blends or polymer dispersions. Though sulfonated ionomers of different rubbers have been reported, the phosphated ionomer has not yet been obtained. This paper deals with the synthesis conditions for the preparation of novel phosphated SBS ionomers via ring-opening reaction of epoxidized SBS with aqueous dialkali salt of hydrogen phosphate solution. Characterization of the ionomers was carried out with FTIR spectrophotometry and TEM. Their oil and water absorbencies, emulsifying property, dilute solution property and mechanical properties, as well as blends with polypropylene and use as compatibilizer for blending SBS and oil resistant chlorohydrin rubber (CHR) were studied, in order to obtain a polar functionalized SBS with increasing interests for many applications, such as adhesive for polar substance, emulsifier, compatibilizer for blends of polar and nonpolar substances and so on.

2 Experimental

2.1 Materials

SBS of YH791 type is a product made by Yue-Yang Synthetic Rubber Factory in China with molecular weight about 100,000 and polystyrene blocks content of 30 wt%. Polypropylene was supplied by Ba-Lin Petroleum Chemicals Co., China. Dialkali salts of hydrogen phosphate were obtained by a reaction of phosphoric acid with alkali hydroxide at an equivalent ratio of 1:2. 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.

2.2 Epoxidation of SBS in the Presence of a Phase Transfer Catalyst

Epoxidation of SBS was carried out via reaction of SBS in cyclohexane solution (SBS concentration = 11 g/100 mL) with performic acid formed from 85% aqueous HCOOH

and 30% aqueous H$_2$O$_2$ solution *in-situ* at 70°C for 4 h, using 1 wt% poly(ethylene glycol) 600/SBS as a phase transfer catalyst. The molar ratio of H$_2$O$_2$/HCOOH was 1. The product(ESBS) was precipitated and washed several times with 95% ethanol till neutral, followed by drying in a vacuum dryer at 60°C.

2.3 Ring-opening Reaction of ESBS with Na$_2$HPO$_4$ to Form Ionomer

ESBS was first dissolved in toluene to form a solution with a concentration of 14 g/100 mL, into which was added 5 wt% tetraethyl ammonium bromide (TEAB)/ESBS as a phase transfer catalyst and 5 wt% N,N-dimethyl aniline(DMA)/ESBS as a ring-opening catalyst. An aqueous solution of Na$_2$HPO$_4$ and Na$_3$PO$_4$(BP) was then added with vigorous stirring at 75°C for 7 h according to a molar ratio of Na$_2$HPO$_4$/epoxy group at 1.8 and 60 wt% Na$_3$PO$_4$/Na$_2$HPO$_4$. The reaction was then terminated by adding an excessNaOH solution with stirring for 10 min to neutralize the unreacted Na$_2$HPO$_4$. 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, followed by drying the precipitate in vacuum dryer at 60°C.
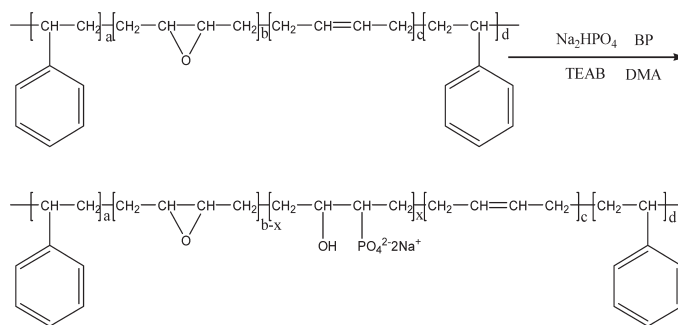
Lithium or potassium phosphated ionomer was prepared by reaction of ESBS with Li$_2$HPO$_4$ or K$_2$HPO$_4$ in a similar way.

2.4 Chemical Analysis

Epoxy group in the ESBS was determined by the HCl-acetone method (19) as follows: About 1 g sample was accurately weighed into an iodometric titration flask. 25 mL of HCl-acetone (1/80 by volume) solution was added. The flask was stoppered and the mixture was stirred until the sample was dissolved. After standing in the dark for 1 h, three drops of phenolphthalein indicator were added and the solution was titrated with standard alcoholic KOH solution to pink color.

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

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

Conversion of epoxy group to phosphate group was obtained by subtraction of two epoxy values determined before and after ring-opening reaction divided by the original epoxy value.

2.5 Characterization

FTIR spectrum of the disodium phosphated SBS ionomer was taken with a Bruker Equinox 55 FTIR spectrophotometer, using a KBr disc, coated with a chloroform solution of the sample, followed by evaporation of solvent. Transmission electron micrograph (TEM) of lead ion neutralized SBS ionomer was obtained by a JEM-100CXII transmission electron microscope, after the disodium phosphated ionomer was treated with lead acetate solution, followed by washing with water and drying. Scanning electron micrographs were taken by JSM−5610 electron microscope, after the broken section of the blend sample was vacuum deposited with golden vapor.

2.6 Oil or Water Absorbency of the Ionomer

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

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

2.7 Solution Viscosity of the Ionomer

Intrinsic viscosity (η) of the ionomers in chloroform was measured by an Ubbelohde viscometer at $25°C$.

2.8 Emulsifying Property of the Ionomer

The emulsifying property can be represented by the emulsifying volume, which was determined as follows: A weighed sample of ionomer was dissolved in 30 mL toluene and then mixed with 70 mL water during vigorous stirring for 5 min. The mixture was poured into a cylinder with a cover and stood overnight. The volume of emulsion was recorded as the emulsifying volume.

2.9 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 with a stretching rate of 250 mm/min. Permanent set was measured as % elongation 3 min after the specimen was broken and reunited.

2.10 Blending of 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 which depends on the amount of PP used. The blend was compression molded at the same temperature under $10-15$ MPa.

2.11 Blending of SBS with Chlorohydrin Rubber (CHR) in the Presence of the Ionomer as Compatibilizer

Blending of SBS with CHR in $1/1$ 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 compression molded at $160°C$ under $10-15$ MPa.

3 Results and Discussion

3.1 Synthesis Conditions for Phosphated Ionomers of SBS

Preliminary experiments showed that it is necessary to use a phase transfer catalyst, a ring-opening catalyst and a pH regulator in the ring-opening reaction of ESBS with Na_2HPO_4, so as to obtain high epoxy group conversion. The results for various factors affecting on the epoxy group conversion stated below were carried out in the conditions described in the above experimental procedure, including the use of tetraethyl ammonium bromide(TEAB) as a phase transfer catalyst, dimethylaniline as a ring-opening catalyst and Na_3PO_4 as a pH regulator.

Because the reaction was carried out in both the aqueous solution of Na_2HPO_4 and toluene solution of ESBS, the ring-opening reaction of ESBS with Na_2HPO_4 to form phosphated ionomer is difficult and may be accelerated by the addition of a phase transfer catalyst. Table 1 shows the effect of tetraethyl ammonium bromide (TEAB) as a phase transfer catalyst on the conversion of epoxy groups to disodium phosphate groups. In the absence of phase transfer catalyst the epoxy conversion is quite low. Conversion of epoxy groups increases with increasing amount of TEAB. The optimum amount is 5 wt% TEAB based on ESBS, as the epoxy conversion increases slowly over 5 wt% TEAB.

Table 1. Effect of amount of DMA and TEAB on epoxy conversion of ESBS

TEAB/ESBS (wt%)	DMA/ ESBS (wt%)	Epoxy conversion (%)
0	5	6.4
3	5	19.6
5	5	30.5
7	5	31.8
5	0	8.9
5	3	20.4
5	5	30.5
5	7	31.4

Table 2. Effect of amount of Na_2HPO_4 and ESBS concentration on epoxy conversion of ESBS

Na_2HPO_4/epoxy group (molar ratio)	ESBS concentration (g/100 mL)	Epoxy conversion (%)
1.6	14	24.6
1.8	14	30.5
2.0	14	27.4
1.8	10	13.6
1.8	12	22.8
1.8	14	30.5
1.8	16	Gel

N,N-dimethylaniline(DMA) can be used as a catalyst for the ring opening reaction of epoxy group with carboxylic acid, thus it was tested as a catalyst for the ring-opening reaction of epoxy groups of ESBS with $Na_2HPO_4$to form phosphated ionomer of SBS. The epoxy conversion is low without the use of DMA. Addition of DMA can increase the epoxy conversion. Over 5 wt% DMA, the epoxy conversion increases slowly, as shown in Table 1.

The effect of molar ratio of Na_2HPO_4/epoxy group on the conversion of epoxy groups of ESBS is shown in Table 2. The conversion increases with increasing molar ratio of Na_2HPO_4/epoxy group. The optimum molar ratio is 1.8/1, over which the conversion decreases gradually. The optimum molar ratio much higher than 1/1 is attributed to the heterogeneous reaction.

Table 2 also indicates that with increasing ESBS concentration, the conversion of epoxy groups into $Na_2PO_4^-$ groups clearly increases from 10 to 14 g/100 mL. The epoxy conversion can reach about 31% at ESBS concentration of 14%. However, the reaction solution becomes too viscous and difficult to stir and forms a gel during the reaction, when the ESBS concentration is over 14 g/100 mL. Hence, the optimum ESBS concentration is 14 g/100 mL.

Table 3 shows the effect of reaction temperature on the conversion of epoxy groups to phosphate groups. The reaction rate increases with a temperature below 75°C, and then falls down. The optimum temperature is 75°C. In all probability, a higher temperature may induce side reactions.

Table 3. Effects of reaction temperature and time on the epoxy conversion

Temperature (°C)	Time (h)	Epoxy conversion (%)
65	7	20.7
70	7	26.8
75	7	30.5
80	7	28.6
75	5	18.9
75	6	25.1
75	7	30.5
75	8	31.6

Table 4. Effect of Na_3PO_4 amount on epoxy conversion

Na_3PO_4/Na_2HPO_4 (wt%)	Epoxy conversion (%)
0	18.9
20	22.4
40	26.5
60	30.5
80	27.2

Table 3 also shows that the epoxy group conversion increases rapidly with reaction time before 7 h, and then gradually. In order to obtain a higher conversion of epoxy groups, a long reaction time is necessary.

It was found that after the addition of Na_3PO_4 to the reaction mixture to adjust the pH of the reaction, the conversion increases with increasing the amount of Na_3PO_4, till Na_3PO_4/Na_2HPO_4 weight ratio of 60 wt%, as shown in Table 4. Since Na_3PO_4 is more alkaline than Na_2HPO_4, this indicates that slightly alkaline medium is beneficial to this ring-opening reaction.

3.2 Characterization of the Phosphated Ionomer of SBS

The FTIR spectrum of the $Na_2PO_4^-$ groups containing SBS (Figure 1) shows that absorption peaks exist at 910, 968 and 730 cm^{-1} for the double bonds of polybutadiene segments and those at 699, 1450 cm^{-1} for the phenyl groups. The absorption peaks at 810 and 880 cm^{-1} indicate the unreacted epoxy groups. The broad absorption peak at 3450 cm^{-1} exists for the OH group, which was formed simultaneously during a ring-opening reaction of epoxy groups with Na_2HPO_4. The existence of absorption peaks at 1160 and 1066 $cm^{-1}$are attributed to the P=O and P-O-C of the phosphate groups in the main chains. Thus, the IR spectrum indicates the functional groups of the phosphated SBS ionomer.
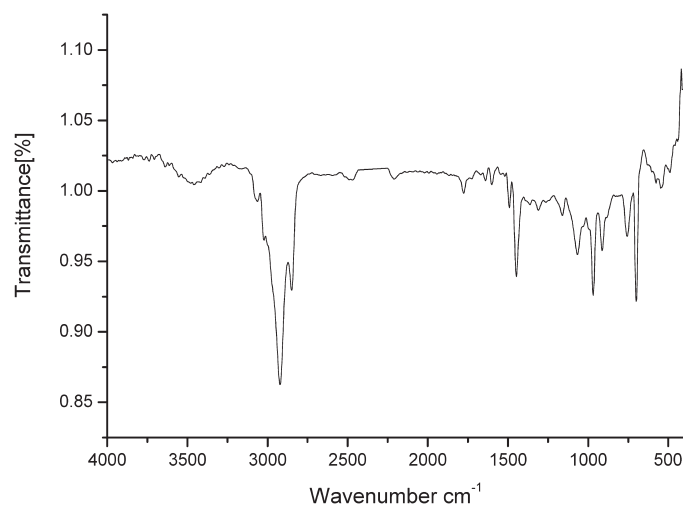

Fig. 1. FTIR spectrum of phosphated SBS ionomer.

Fig. 2. TEM micrograph of lead phosphated SBS ionomer with a magnification of 50000X.

Transmission electron micrograph (Figure 2) shows dark spots in the specimen of lead phosphated SBS ionomer, which was obtained by treating the disodium phosphated ionomer with lead acetate in solution for 24 h, followed by washing with water and drying. Since the lead ions can absorb the electrons and the ions associate into ionic domains, the latter appears as dark spots under TEM. The spots exhibited somewhat needle-like shape with quite different lengths in the range of 10^1 nm order. This needle shape is quite different from the ordinary sphere shape of the sulfonated ionomer. Probably this phenomenon is attributed to the existence of two negative charges of the phosphate group in the disodium phosphated ionomer. When the sodium ions were exchanged with lead ions before TEM examination, the lead ion can combine with one or two negative charges of one phosphate group. The lead ion may interact with two negative charges in one phosphate group or interact with each one negative charge in two phosphate groups. The TEM micrograph demonstrates the product to be an ionomer, which is also a nanocomposite in molecular level.

3.3 Some Properties of the Phosphated Ionomer of SBS

The ionomer can absorb water because it contains the hydrophilic $Na_2PO_4^-$ group. Table 5 indicates that with increasing

Table 5. Effect of ionic group content on water absorbency, oil absorbency and dilute solution viscosity of the ionomers

Ionic group content (mmol/g)	Water absorbency (%)	Kerosene absorbency (%)	$(\eta)/(mL/g)$
0.38	24.6	664	154
0.64	98.5	347	189
0.96	197	125	249
1.16	298	32.2	304

ionic groups, water absorbency increases, more obviously over 0.4 mmol ionic groups/g. The water absorbency of the ionomer containing phosphate groups is much higher than that of the ionomer containing sulfonate groups, even more than 10 times (20).

Table 5 also shows that the ionomer offers good kerosene resistant properties. The oil absorbency of the ionomer decreases with increasing the ionic groups. At an ionic group content about 1.16 mmol/g, the ionomer absorbs only 32% kerosene. This fact is attributed to the association of the ionic groups in the nonpolar oil, resulting in oil resistance.

Intrinsic viscosity (η) of the ionomers in chloroform increases with increasing ionic groups, as also shown in Table 5. It increases more sharply over 0.6 mmole ionic group/g. This phenomenon can be explained by the fact that the more the ionic groups, the more the association between the ionic groups of the ionomer macromolecules, resulting in higher resistance to flow or higher viscosity.

Table 6 denotes that with increasing the ionic potential of the cations in the ionomer, the water absorbency and the intrinsic viscosity of the ionomer increase, whereas the oil absorbency decreases. The higher the ionic potential of the cation of the ionomer, the higher the repulsive force between the phosphate groups in the macromolecule and the more straight the macromolecules, thus resulting in the higher viscosity.

Since the ionomer contains both hydrophilic $Na_2PO_4^-$ groups and hydrophobic SBS segments, it exhibits amphiphilic properties and can emulsify toluene and water system. Table 7 shows that the emulsifying volume increases with increasing ionic groups, due to the increase of emulsifying centers. The emulsifying volume reaches over 84 mL, when the ionic groups reaches 1.16 mmol/g. The emulsifying property of the ionomer containing phosphate groups is much better than that of the ionomer containing sulfonate groups (20). The emulsifying volume of the latter with about the same ionic group content is only 38 mL.

The emulsifying volume increases with increasing the ionic potential of the cation, as also shown in Table 7; this is because increasing the ionic potential of the cations in the ionomer, the water absorbency increases.

3.4 Mechanical Properties of the Disodium Phosphated Ionomer

It is better to process the ionomer in the presence of zinc stearate, so as to lower the melt viscosity. Table 8 shows the tensile strength, ultimate elongation and permanent set of the ionomer in the presence of various amounts of zinc stearate. It can be seen that tensile strength and ultimate elongation increased with increasing amounts of zinc stearate as an ionic plasticizer up to 10%, whereas in the case of the ionomer containing 15% zinc stearate, excess zinc stearate separated out as a liquid during melt mixing and molding. The effect of zinc stearate on the mechanical properties of the ionomer can be interpreted as follows: with

Table 6. Effect of cations on water absorbency, oil absorbency and dilute solution viscosity

Cations	Ionic potential	Ionic group content/(mmol/g)	Water absorbency (%)	Kerosene absorbency (%)	(η) (mL/g)
Li^+	1.46	1.06	321	26.4	338
Na^+	1.03	1.16	298	32.2	304
K^+	0.75	1.21	271	69.5	273

Table 7. Effect of ionic group content and kind of cation on emulsifying property of ionomer

Cations	Ionic potential	Ionic group content/ (mmol/g)	g ionomer/ 100 mL	Emulsifying volume (mL)
Na^+	1.03	0.38	0.2	34.5
Na^+	1.03	0.64	0.2	48.2
Na^+	1.03.	0.96	0.2	76.4
Na^+	1.03	1.16	0.2	84.2
Li^+	1.46	1.06	0.1	83.5
Na^+	1.03	1.16	0.1	77.1
K^+	0.75	1.21	0.1	71.2

an increasing amount of zinc stearate, more zinc stearate is distributed in the ionic domains of the ionomer, thus making the size of domains diminish and the number of domains or the number of physical crosslinks increase, resulting in the increase of tensile strength. However, excess zinc stearate will separate out. Uniform distribution of ionic domains in the presence of zinc stearate also makes the exchange of ionic bonds easier, thus increasing the ultimate elongation of the ionomer and also the permanent set. However, the permanent set for the ionomer with 10% zinc stearate is still lower and within the range of thermoplastic elastomer ($<50\%$).

Table 9 indicates that in the presence of 10% zinc stearate, with increasing ionic group content, both tensile strength and ultimate elongation increase due to the increased number of ionic domains formed in the ionomers with higher $Na_2PO_4^-$ group content. The permanent set increases with increasing ultimate elongation, but still within the range of thermoplastic elastomer. However, with increasing ionic groups exceeding 0.95 mmole/g, the tensile strength, ultimate elongation and permanent set of the ionomer all decrease. This fact can be interpreted as the excess physical crosslinks formed by too much or too large ionic domains. The mechanical properties

Table 8. Effect of amount of zinc stearate on mechanical properties of disodium phosphated SBS ionomers[a]

Zinc stearate/ionomer (wt%)	0	5	10
Tensile strength (MPa)	12.1	15.6	17.8
Ultimate elongation (%)	981	1060	1580
Permanent set (%)	11	18	27

[a]Ionic group content of ionomer is 0.95 mmol/g.

Table 9. Effect of ionic group content on mechanical properties of phosphated SBS ionomer

Ionic group content (mmol/g)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	9.14	420	16
0.36	12.9	846	18
0.61	15.7	1210	25
0.95	17.8	1580	27
1.10	15.4	1140	19

of the phosphated SBS ionomer are better than those of the maleated SBS ionomer (21). This may be attributed to stronger association force of the disodium phosphate ions than that of the maleate ions.

3.5 Blends of Disodium Phosphated SBS Ionomer with Polypropylene

Table 10 lists the mechanical properties of the disodium phosphated SBS ionomer/PP blends with different compositions. It can be seen that with increasing PP, the blend changes its behavior from thermoplastic elastomer to toughened plastics. Figure 3 shows the relationship between tensile strength and composition of the blends. The straight line represents the theoretical additive relationship between tensile strength and composition of the blends. Obviously, except for the blend containing 75% ionomer, a synergism was observed for tensile strength of the ionomer/PP blends, i.e., tensile strength of the blend is higher than the calculated sum of tensile strength contributed by the two components. It may be attributed to the thermoplastic interpenetrating polymer network (IPN) formed in the blend, because both the ionic domains and the glassy domains in the SBS

Table 10. Effect of ionomer content on mechanical properties of ionomer/PP blends

Ionomer/PP (wt ratio)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0/100	35.2	1.20	/
25/75	31.9	5.64	/
50/50	27.9	141	18
75/25	21.8	996	23
100/0	17.8	1580	27
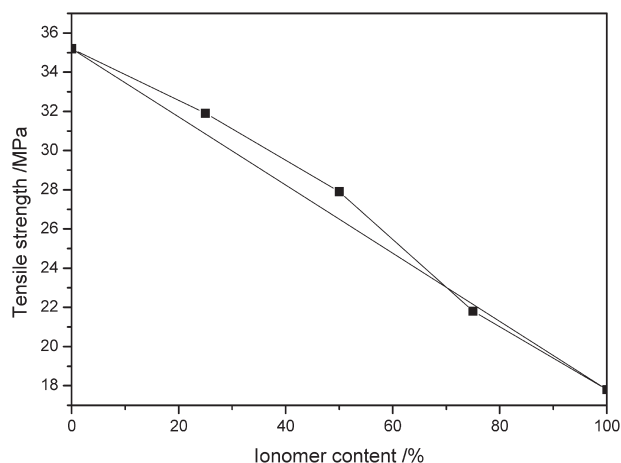
Fig. 3. Relationship between ionomer content and tensile strength of the ionomer/PP blends.

Table 11. Effect of amount of ionomer[a] on mechanical properties of SBS/CHR blends

Ionomer/ blend (wt%)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	8.64	856	16
1	11.4	981	18
2	12.6	1320	20
3	14.4	1500	22
4	13.2	1560	25
5	12.4	1490	24

[a]Ionic group content of the ionomer used is 1.10 mmol/g.

ionomer and also the crystalline regions or crystallites of the PP can be considered as physical crosslinks. Since there are some similarities between methyl groups-containing amorphous phase of PP and vinyl groups-containing SBS phase, the components show certain affinity for each other, and during melting the segments of different macromolecules diffuse into each other at interfaces between the two phases, where the three physical crosslinks penetrate into each other and enhance the compatibility of the two components, thus increasing the interfacial adhesion and the ability to transfer stress through phases, resulting in synergism in strength (22).

The blend with weight ratio of PP/SBS at 1/1 showed the toluene absorbency of 6.4%, whereas SBS is soluble in toluene. This fact indicates that the two components are quite compatible due the enhanced compatibilization of thermoplastic interpenetrating network formed from the crystalline PP domains and the polystyrene glass domains and ionic domains in the blend.

3.6 Blending of SBS with Chlorohydrin Rubber (CHR) using Disodium Phosphated SBS Ionomer as Compatibilizer

The phosphated SBS ionomer can be used as a compatibilizer for the blending of SBS with chlorohydrin rubber, which is a polar, oil resistant and vulcanizable elastomer. When a small amount of the ionomer is added to the blend of SBS and CHR in a weight proportion of 50/50, the mechanical properties of the blend are improved. In particular, when the ionomer added reached 3 wt% of the blend, both the tensile strength and the ultimate strength of the blend increased to 1.7 times, as shown in Table 11. However, the permanent set is kept at about 20%, which is within the range of thermoplastic elastomer. Thus the blends behave as thermoplastic elastomers. The improvement of mechanical properties of the blend by the small amount of ionomer may be attributed to the interfacial adhesion via the ionomer, because on the one side, the SBS backbone of the ionomer is miscible with the SBS phase and on the other side, there exists an ion-dipole interaction between ether linkage of CHR and the ionic groups of the ionomer. But, 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 the surface of SBS phase were shielded by the ionic groups of the excess ionomer used.

The effect of the disodium phosphated SBS ionomer as compatibilizer is stronger than that of the maleated SBS
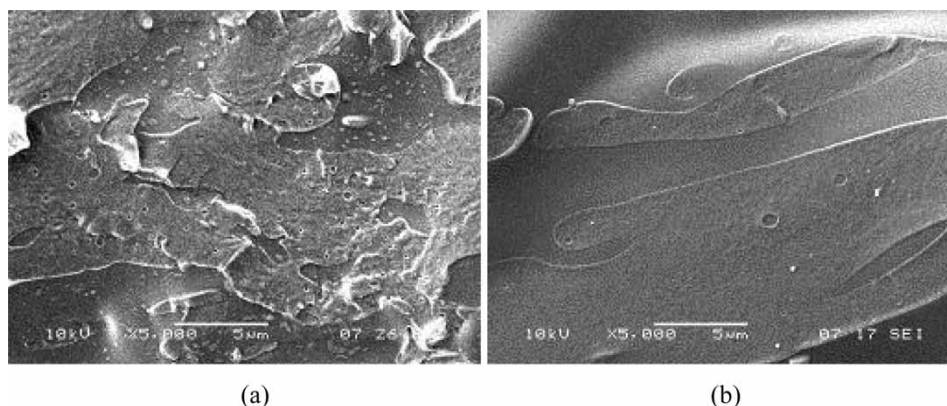

(a)　　　　　　　　　　　　(b)

Fig. 4. SEM micrographs of SBS/CHR blends without (a) and with (b) 3% ionomer with magnification of 5000X.

Table 12.   Effect of ionomer as a compatibilizer on kerosene absorbency of SBS/CHR blends

Ionomer/blend (wt%)	Kerosene absorbency (%)
0	89.6
3	52.4

ionomer (21). In the former case, 3% ionomer can raise both the tensile strength and ultimate elongation about 1.7 times, whereas in the latter case, 3% ionomer can only raise these mechanical properties 1.2 times (21). This fact may be attributed to the stronger ion-dipole interaction of the disodium phosphate ion with the ether linkage of CHR than that of the maleate ion.

The enhanced compatibility of the two components by the ionomer can be demonstrated by SEM. SEM micrographs of the surface of broken sections of the blends of SBS/CHR with or without addition of the ionomer as compatibilizer are shown in Figure 4. The surface of the broken section of the blend containing the ionomer is smoother than that without the ionomer. Thus, it implies that the ionomer improves the interfacial adhesion between the surfaces of the two phases.

It was noted that the SBS/CHR(1/1) blend without the ionomer as compatibilizer absorbed kerosene about 90%, whereas that with the ionomer absorbed about 52% kerosene (Table 12). This also indicates that the ionomer enhances the compatibility of SBS and CHR in the blend, which exhibits higher oil resistance.

4   Conclusions

A novel method for preparation of phosphated ionomer of SBS was developed by a ring-opening reaction of epoxidized SBS with Na_2HPO_4 The optimum conditions are: at ESBS concentration of 140 g/L, molar ratio of Na_2HPO_4/epoxy group at 1.8, weight ratio of TEAB/ESBS at 5%, weight ratio of DMA/ESBS at 5% and weight ratio of Na_3PO_4/Na_2HPO_4 at 60% and at 75°C for 8 h. The FTIR spectrum demonstrated the characteristic groups of the phosphated SBS ionomer and the TEM micrograph of the lead phosphated ionomer demonstrated the presence of ionic domains, as dark spots. With increasing ionic groups content or the ionic potential of the cation of the ionomer, the water absorbency, emulsifying volume and the dilute solution viscosity of the ionomer increase, whereas its oil absorbency decreases. The ionomer possesses excellent emulsifying property, as compared with the sulfonated SBS ionomer. These properties demonstrated the amphiphilic nature of the ionomer. The disodium phosphated ionomers in the presence of 10% zinc stearate shows better mechanical properties than original SBS. The tensile strength and ultimate elongation increase with increasing ionic group of the ionomer up to 0.95 mmol/g. When the ionomer was blended with polypropylene, a synergistic effect occurs 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 polypropylene containing crystalline domains. The ionomer behaves as a compatibilizer for blending equal amount of SBS and oil-resistant CHR through the ion-dipole interaction. In the presence of 3% ionomer, the blend exhibits much better mechanical properties and kerosene resistance than the blend without the ionomer and behaves as oil resistant thermoplastic elastomer. SEM micrographs indicate increased compatibility between the two components in the presence of the ionomer.

5   Acknowledgement

6   References

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