

Synthesis and Characterization of Maleated Ionomers via Ring-Opening Reaction of Epoxidized Styrene-Butadiene Rubber with Potassium Hydrogen Maleate and Study of their Behavior as Compatibilizer

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ABSTRACT: A novel method for synthesizing maleate ionomer of (styrene-*co*-butadiene) rubber (SBR) from epoxidized SBR was developed. The epoxidized SBR was prepared via epoxidation of SBR with performic acid formed *in situ* by H₂O₂ and formic acid in cyclohexane. The maleated ionomer was obtained by ring-opening reaction of the epoxidized SBR solution with an aqueous solution of potassium hydrogen maleate. The optimum conditions were studied. It was found that it is necessary to use phase transfer catalyst and ring-opening catalyst for enhancing the epoxy group conversion. To obtain 100% conversion addition of dipotassium maleate is important. The product was characterized by FTIR spectrophotometry and transmission electron microscopy (TEM). The results showed that the product was really an ionomer with domains of maleate ionic groups. Some properties of the ionomer, such as water absorbency, oil absorbency and dilute solution behavior were studied. With increasing ionic groups, the water ab-

sorbency of the ionomer increases, whereas the oil absorbency decreases. The dilute solution viscosity of the ionomer increases abruptly with increasing ionic group content. The ionomer can be used as a compatibilizer for the blends of SBS and chlorosulfonated polyethylene (CSPE). Addition of a small amount of the ionomer to the blend can enhance the mechanical properties of the blends. 3 wt % ionomer based on the blend can increase the tensile strength and ultimate elongation of the blend nearly twice. The compatibility of the blends enhanced by adding the ionomer was shown by scanning electron microscopy. The blend of equal parts of SBS and CSPE compatibilized by the ionomer behaves as an oil resistant thermoplastic elastomer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 792–798, 2006

Key words: ionomer; epoxidation, ring-opening reaction, maleation, compatibilizer, (styrene-*co*-butadiene) rubber

INTRODUCTION

Styrene-butadiene random copolymer is prepared from emulsion polymerization of styrene and butadiene and can be vulcanized to form a chemically crosslinked rubber. Since it is of a nonpolar nature, its modification to form thermoplastic elastomer with polar groups has attracted interest, to widen its uses. Ionomer is a kind of polymer containing less than 10% ionic groups and shows characteristic properties due to the presence of ionic domains. Ionomers of sulfonated rubbers, such as ethylene-propylene-diene copolymer and butyl rubber, are thermoplastic elas-

tomers with ionic domains as physical crosslinks.^{1–4} Ionomers of maleated and sulfonated styrene-butadiene-styrene triblock copolymer (SBS) were prepared by De and coworkers⁵ through sulfonation of maleated SBS, a Kraton product with maleic anhydride content below 2 wt %. Xie and coworkers⁶ used sodium ionomer of maleated SBS as self-emulsifier for graft copolymerization of SBS with acrylamide. The ionomer of maleated SBS was obtained by maleation of SBS in solution with maleic anhydride and benzoyl peroxide, followed by neutralization with metallic acetate or hydroxide. However, the reaction mixture containing benzoyl peroxide must be carried out under nitrogen atmosphere, and crosslinking reaction or gel formation may occur because of the radicals formed by benzoyl peroxide, if the reaction conditions are not well controlled. Jacobi et al.⁷ recently reported the epoxidation of (styrene-*co*-butadiene) rubber (SBR) using performic acid formed *in situ* and showed that

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the reaction was highly dependent upon the H_2O_2 concentration, time, and temperature. Studies related to the addition of nucleophilic reagents, such as acid, amine, and alcohol, onto epoxidized polydiene were performed by Soutif et al.,⁸ Jayawardena et al.,⁹ and Derouet et al.,¹⁰ respectively. Soutif et al.⁸ added naphthylacetic acid to epoxidized 1,4-polyisoprene using tetramethyl ammonium salt of the acid as a catalyst, and obtained about 40% conversion at 100°C for 48 h. Derouet et al.¹⁰ modified epoxidized 1,4-polyisoprene via ring-opening reaction with alcohol using cerium ammonium nitrate as a catalyst. Recently, Xie et al.¹¹ synthesized quaternary ammonium ionomer of SBS via ring-opening reaction of epoxidized SBS with triethylamine hydrochloride with 100% conversion. Hara et al.¹² indicated the miscibility enhancement via ion-dipole interaction between polystyrene ionomer and poly(alkylene oxide).

This paper deals with the synthesis conditions for the preparation of maleate SBR ionomer via epoxidation of SBR in solution in the presence of phase transfer catalyst, followed by ring-opening reaction of epoxidized SBR (ESBR) with potassium hydrogen maleate (PHM) without nitrogen atmosphere and its characterization with FTIR, transmission electron microscopy (TEM) as well as its water absorbency, oil absorbency and dilute solution properties and behavior as compatibilizer in blending of chlorosulfonated polyethylene (CSPE) with SBS via ion-dipole interaction.

EXPERIMENTAL

Materials

SBR 1500 is a product made by Lanzhou Chemical Industrial Company in China with Mooney viscosity of 52 and styrene content of 23.5%. Lead acetates, acetone, formic acid (85%), hydrogen peroxide (30%), maleic anhydride, cyclohexane, tetraethyl ammonium bromide (TEAB), *N,N*-dimethylaniline (DMA), poly(ethylene glycol) with molecular weight of 600 (PEG 600), and ethanol were chemically pure. Antioxidant 264 (2,6-di-*tert*-butyl-4-methylphenol) was an industrial product. Hydrochloric acid and KOH were analytical reagents. PHM and dipotassium maleate (DPM) were prepared by mixing aqueous solution of KOH with maleic anhydride in molar ratio of 1/1 and 2/1, respectively, for half an hour at room temperature.

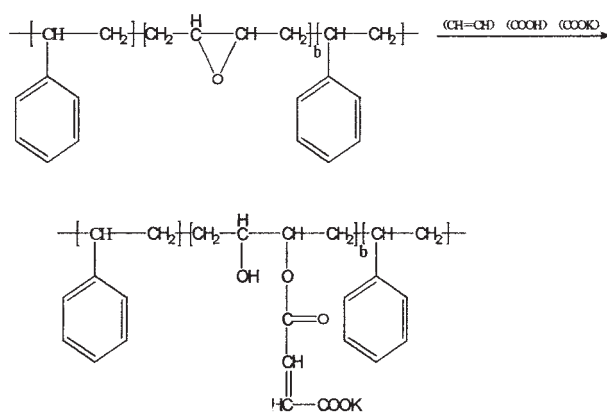
Epoxidation of SBR

Epoxidation of SBR was carried out via reaction of SBR in cyclohexane solution at a concentration of 11 g/100 mL with performic acid formed by HCOOH and 30% aqueous H_2O_2 solution *in situ* at 70°C for 2 h,

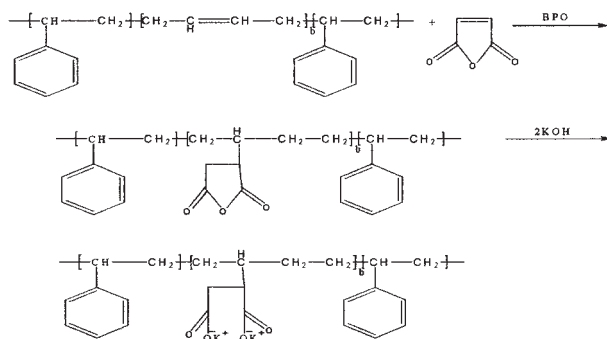
using 5 wt % PEG/SBR as a phase transfer catalyst. The molar ratio of $\text{H}_2\text{O}_2/\text{HCOOH}$ was 1. The product was precipitated and washed several times with 95% ethanol containing 0.5% antioxidant 264, followed by drying in a vacuum dryer at 60°C.

Ring-opening reaction of epoxidized SBR with PHM to prepare potassium maleate ionomer of SBR

The ionomer was made by the ring-opening reaction of epoxy groups in the ESBR with PHM as follows: ESBR was first dissolved in toluene with stirring to form a solution with a concentration of 13 g/100 mL, into which were added 5 wt % dimethylaniline as ring-opening reaction catalyst and 15 wt % PEG 600 based on ESBR as a phase transfer catalyst. An aqueous solution of PHM and DPM according to a molar ratio of PHM/epoxy group at 1.8 and a weight ratio of DPM/PHM at 20% was then added with vigorous stirring at 70°C for 7 h. The reaction was terminated by adding a small amount of acetone solution containing antioxidant 264. The mixture was washed with distilled water to neutral, and then precipitated by ethanol, followed by drying in vacuum dryer at 60°C



This product containing maleate ion is different from that obtained by ordinary reaction of (styrene-butadiene) rubber with maleic anhydride in the presence of benzoyl peroxide or called maleic anhydride grafting, the equation of which is as follows:



The latter product contains dipotassium succinate groups, but not potassium maleate group with double bond in the former product.

Chemical analysis

Epoxy group in the ESRB was determined by the HCl-acetone method¹³ as follows. About 1 g sample was accurately weighed into an iodometric titration flask. 25 mL of HCl-acetone (1/80) 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 was added and the solution was titrated with standard alcoholic KOH solution to pink color.

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

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

$$\text{Epoxy group wt \%} = E \times 42\%$$

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

Characterization

FTIR spectrum of the maleated SBR ionomer 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. Transmission electron micrograph of SBR ionomer was obtained by a JEM-100CXII transmission electron microscope, after the potassium ionomer was treated with lead acetate solution, followed by washing. Scanning electron micrographs of the broken section of the blends were taken by JSM -5610 electron microscope.

Oil or water absorbency of the ionomer

Oil absorbency or water absorbency was determined by immersing an accurately weighed sample (W_b) in diesel 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).

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

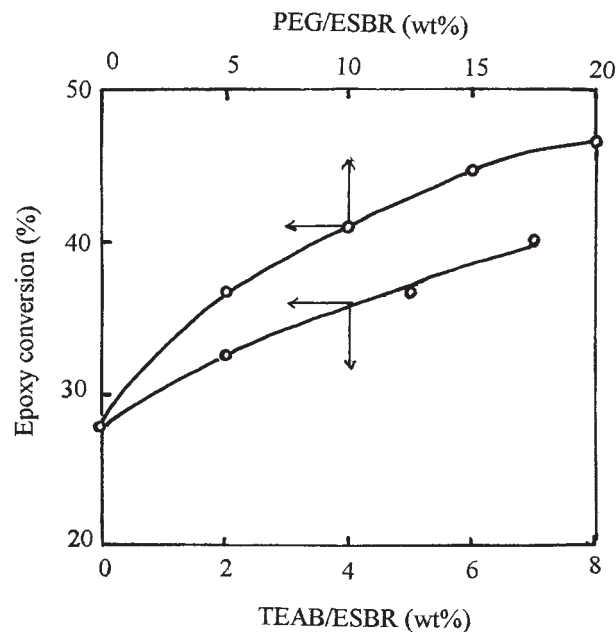


Figure 1 Effects of two kinds of phase transfer catalysts on the epoxy conversion.

Solution viscosity of the ionomer

Dilute solution viscosity (η_r/C) of the ionomers in a mixed solvent of toluene/methanol (9/1) at about 0.1 g/100 mL concentration was measured by an Ubbelohde viscometer at 25°C, where η_r is the relative viscosity and C the concentration of the solution.

RESULTS AND DISCUSSION

Synthesis conditions for ring-opening reaction of epoxy groups in the ESRB with PHM

The solubility of PHM in water is much higher than that of sodium hydrogen maleate. Hence the PHM was used in ring-opening reaction with ESRB. The ESRB concentration was used as 130 g/L toluene, because it is difficult to carry out the ring-opening reaction in a concentration higher than 130 g/L toluene, as the viscosity of the solution is too high and stirring is impossible at the end of the reaction.

Since the reaction is carried out between toluene solution of ESRB and the aqueous solution of PHM, it seems to be necessary to use a phase transfer catalyst. Two phase transfer catalysts were chosen to be tested, namely, TEAB and PEG with molecular weight of 600. Figure 1 shows that with increasing TEAB or PEG amount, the conversion of epoxy groups increases. PEG used as a phase transfer catalyst seems to be better than TEAB with respect to their molar ratios. Though the weight amount of PEG is higher than that of TEAB, but the molar amount of the former is lower than that of the latter.

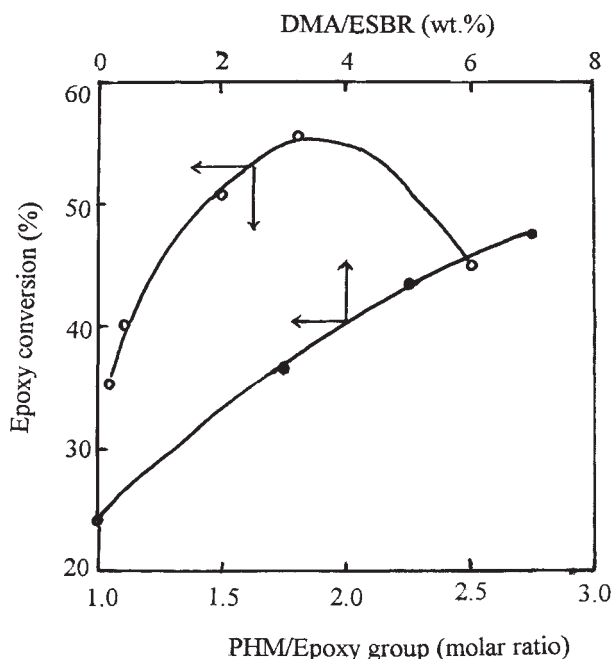


Figure 2 Effects of *N,N*-dimethyl aniline amount and molar ratio of potassium hydrogen maleate/epoxy group on the epoxy conversion.

The ring-opening catalyst for reaction of epoxy group with carboxylic acid, such as *N,N*-dimethyl aniline (DMA), was also tested. It is shown in Figure 2 that the conversion of epoxy groups increases with DMA amount more effectively than with the amount of the phase transfer catalyst. The conversion of epoxy groups was raised nearly twice, when 5% dimethylaniline was added as a catalyst.

The molar ratio of PHM/epoxy group is also important in determining the conversion of epoxy groups, as shown in Figure 2. With increasing the molar ratio, the conversion increases till a molar ratio of 1.8 and then decreases. Excess reagent seems necessary to obtain high conversion, because the higher the concentration of PHM, the higher the rate of reaction. However, excess reagent may cause side reaction and gelation.

If some alkaline substance, such as DPM, was added during the ring-opening reaction, the conversion of the epoxy group rises remarkably, especially over 10 wt % of DPM/PHM as shown in Figure 3. Since DPM is more alkaline than PHM, the reaction would be better carried out in a comparatively more alkaline medium than that containing PHM only.

Figure 4 indicates that 70°C is the optimum reaction temperature for the ring-opening reaction of epoxy groups to form maleate ion groups, both in the presence and absence of DPM. The conversion of epoxy groups increases with reaction temperature from 60 to 70°C. Over 70°C the conversion decreases.

The conversion of epoxy group increases with time, whether in the presence or absence of DPM, as shown

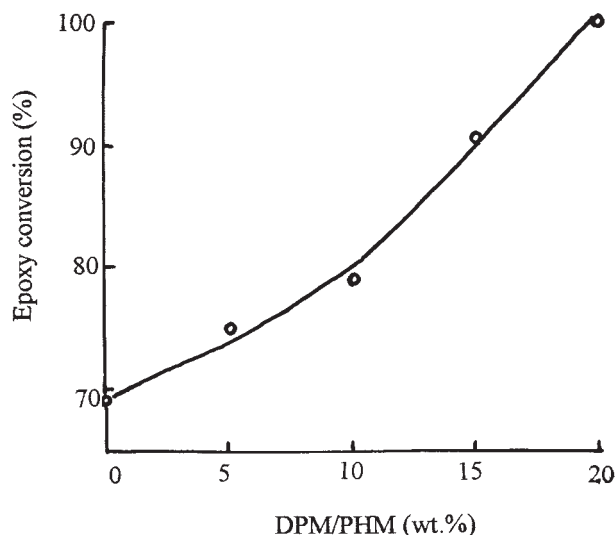


Figure 3 Effects of weight ratio of dipotassium maleate/potassium hydrogen maleate on epoxy conversion.

in Figure 5. The conversion of epoxy group in ESBR can reach 100% at 70°C for 7 h with the following optimum conditions: at ESBR concentration of 130 g/L, molar ratio of PHM/epoxy group at 1.8, weight ratio of DPM/PHM = 20/100, weight ratio of DMA/ESBR at 5%, weight ratio of PEG/ESBS at 15%

Characterization of the potassium maleated ionomer of SBR

The FTIR spectrum (Fig. 6) of the potassium maleated groups containing SBR showed that absorption peaks

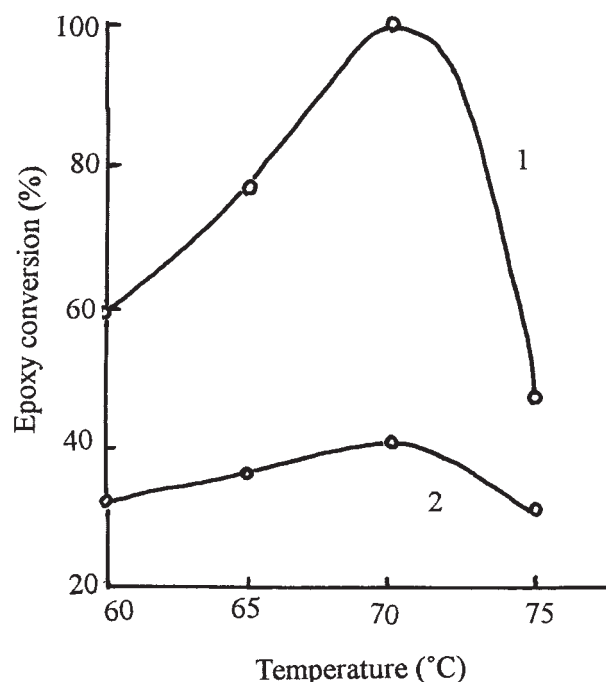


Figure 4 Effect of reaction temperature on epoxy conversion (1, in the presence of DPM; 2, in the absence of DPM).

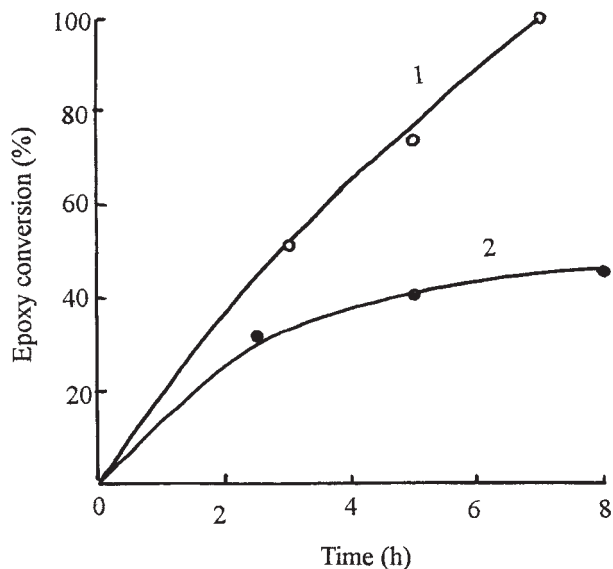


Figure 5 Effect of reaction time on epoxy conversion (1, in the presence of DPM; 2, in the absence of DPM).

at 810, 880 cm^{-1} for the epoxy groups disappeared. There exist absorption peaks at 910, 968, and 731 cm^{-1} for the double bonds of polybutadiene segments and those at 699, 1449, and 1311 cm^{-1} for the phenyl groups. The broad absorption peak at about 3450 cm^{-1} exists for OH group, which was formed during ring-opening reaction of epoxy groups with PHM. The existence of absorption peaks at 1600, 1260, and 1725 cm^{-1} are attributed to COO^- ion, C—O, and C=O groups, respectively. The weak absorption peak of the double bond next to carbonyl groups at 1602 cm^{-1} is overlapped by that for COO^- group. Thus the FTIR spectrum shows the functional groups of the maleate ionomer of SBR.

Transmission electron microphotograph (Fig. 7) shows the black spots in the specimen of potassium

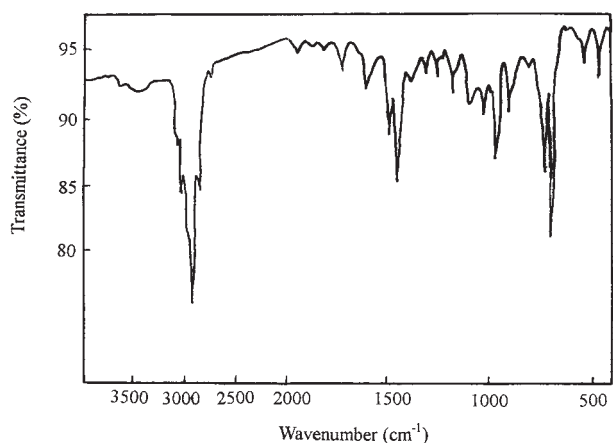


Figure 6 FTIR spectrum of the potassium maleate ionomer of SBR.

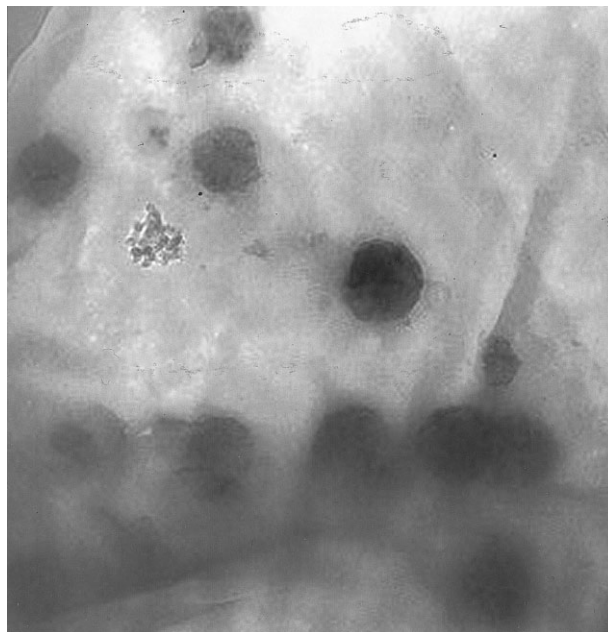


Figure 7 TEM microphotograph the lead maleate ionomer of SBR (with a magnification of 27,500 \times).

maleated SBR ionomer, after the potassium ions were substituted by lead ions. Since the lead ions can absorb the electrons under TEM and the ions associate into clusters, the latter appear as dark spots. Thus the TEM demonstrates that the product obtained is an ionomer.

Some properties of the potassium maleated ionomer of SBR

The ionomer can absorb water, because it contains the hydrophilic potassium maleate ion group. Table I indicates that with increasing potassium maleate ion groups, water absorbency increases. The ionomer containing 1.0 mmol/g can absorb more than half its weight of water.

Table I also shows that the ionomer offers some oil resistant properties. SBR is completely dissolved in diesel oil for 48 h at room temperature, whereas the SBR ionomers containing more than 1.6 mmol ionic groups/g do not dissolve, but absorb oil. The oil ab-

TABLE I
Water Absorbency and Oil Absorbency of the Maleated Ionomer of SBS

Maleated groups (mmole/g)	Water absorbency (%)	Oil absorbency (%)	η_r/C (mL/g)
0	0.2	Soluble	
1.06	60.5	215.4	167.0
1.61	83.7	210.2	183.9
2.07	92.6	142.8	217.6
2.59	99.8	104.9	250.1

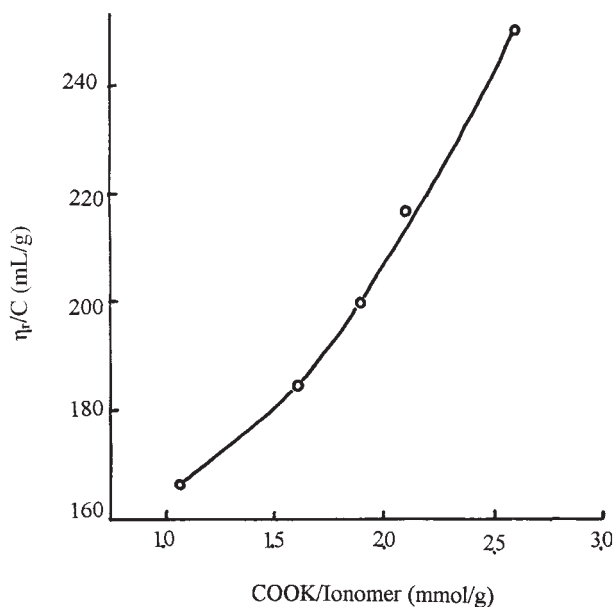


Figure 8 Relationship between dilute solution viscosity and ionic groups content of the SBR ionomer.

sorbency decreases with increasing the ionic groups. This fact is attributed to the association of the ionic groups in the nonpolar oil, resulting in oil resistance.

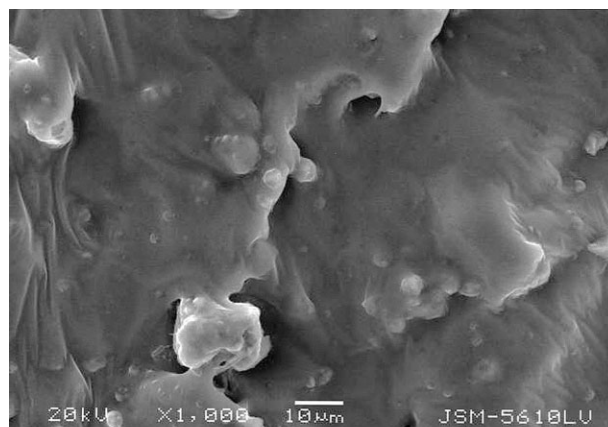
Dilute solution viscosity (η_r/C) of the ionomers in a mixed solvent of toluene/methanol (9/1) increases with increasing ionic groups, as shown in Figure 8. It increases more sharply over 2.0 mmol ionic groups/g. This phenomenon can be explained by the fact that the more the ionic groups, the more the association between the macromolecules of the ionomer is, resulting in higher resistance to flow or higher viscosity.

Behavior of the potassium maleated ionomer as a compatibilizer for SBS/CSPE blends

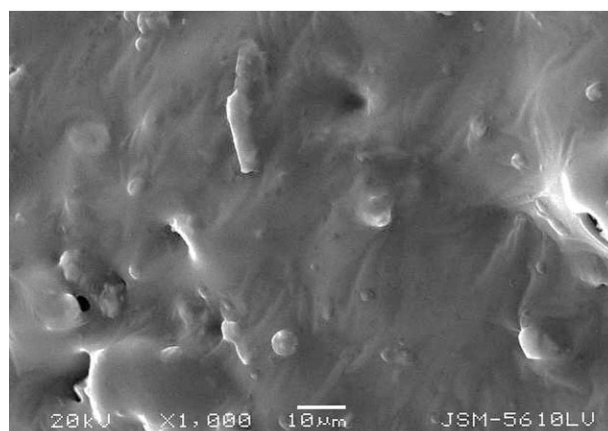
The ionomer was tested as a compatibilizer for blending thermoplastic elastomer SBS and oil resistant CSPE. Table II shows the effect of ionomer amount on the mechanical properties of the blends with weight ratio of SBS/CSPE at 50/50. Both the tensile strength and ultimate elongation of the blend increase with

TABLE II
Effect of Amount of the Ionomer Added on the Mechanical Properties of the SBS/CSPE (50/50 Weight Ratio) Blend

Amount of ionomer added (%)	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)
0	5.3	945	20
1	9.5	2500	17
3	11.6	2360	18
5	10.2	1660	13



(a)



(b)

Figure 9 The SEM micrograph of the broken section of the blend without the compatibilizer (a) and that of the blend with 1% compatibilizer (b) (with a magnification of 1000 \times).

addition of a small amount of the ionomer to the blend. 3% of the ionomer based on the blend seems to be the optimum amount of the ionomer as compatibilizer. This phenomenon may be attributed to the ionic-polar interaction between potassium ion of the ionomer and chlorosulfonate group of CSPE on the one side and to the partial compatibility between SBS phase and SBR part of the ionomer on the other side, thus enhancing the compatibility between SBS and CSPE. Excess ionomer lowers the mechanical properties of the blend. This is because the ionic groups of excess ionomer molecules may associate with the ionic groups of the ionomer molecules on the surface of SBS phase, thus decreasing the interfacial adhesion between the two phases and lowering the compatibilizing effect. The enhanced compatibility of the blends was indicated by SEM micrographs of the broken section of the blends with and without the ionomer added. The surface of the former seems smoother than that of the latter, as shown in Figure 9.

The blend behaves as an oil resistant thermoplastic elastomer with toluene absorbency of -23.5% for 48 h at room temperature.

CONCLUSIONS

A novel method for synthesizing maleate ionomer of SBR from ESBR was developed. The maleated ionomer was obtained by ring-opening reaction of ESBR with an aqueous solution of PHM. It is necessary to use phase transfer catalyst and ring opening catalyst for enhancing the epoxy group conversion. To obtain 100% conversion, addition of DPM to the reaction mixture is important. Characterization by FTIR and TEM showed that the product was really an ionomer with maleate ionic group domains. With increasing ionic groups, the water absorbency of the ionomer increases, whereas the oil absorbency decreases. The dilute solution viscosity of the ionomer increases abruptly with increasing ionic group content. The ionomer can be used as a compatibilizer for the blends of SBS and CSPE. 3 wt % ionomer based on the blend

can increase the tensile strength and ultimate elongation of the blend nearly twice.

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