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Hong-Quan Xie[a]; Wu-Gang Yu[b]; Dong Xie[c]; Da-Ting Tian[d]
[a] Department of Chemistry, Huazhong University of Science and Technology, Wuhan, China [b] Hubei Research Institute of Chemistry, Wuhan, China [c] Department of Biomedical Engineering, Indiana University Purdue University at Indianapolis, [d] School of Chemical and Environmental Engineering, Hubei Institute for Nationalities, Enshi, China

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Synthesis of Maleated Ionomers via Ring-Opening Reaction of Epoxidized (Styrene-Butadiene-Styrene) Triblock Copolymer with Potassium Hydrogen Maleate and Study of their Properties

HONG-QUAN XIE,[1] WU-GANG YU,[2] DONG XIE,[3] and DA-TING TIAN[4]

[1]*Department of Chemistry, Huazhong University of Science and Technology, Wuhan, China*
[2]*Hubei Research Institute of Chemistry, Wuhan, China*
[3]*Department of Biomedical Engineering, Indiana University Purdue University at Indianapolis,*
[4]*School of Chemical and Environmental Engineering, Hubei Institute for Nationalities, Enshi, China*

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A novel method for synthesizing maleated ionomer of (styrene-butadiene-styrene) triblock copolymer (SBS) from epoxidized SBS was developed. The epoxidized SBS was prepared via epoxidation of SBS with performic acid formed in situ by 30% H_2O_2 and formic acid in cyclohexane in the presence of polyethylene glycol 600 as a phase transfer catalyst. The maleated ionomer was obtained by a ring-opening reaction of the epoxidized SBS solution with an aqueous solution of potassium hydrogen maleate. The optimum conditions for the ring-opening reaction and some properties of the ionomers were studied. It is necessary to use phase transfer catalyst, ring-opening catalyst and a pH regulator (dipotassium maleate) for obtaining the epoxy group conversion over 90%. The product was characterized by FTIR spectrophotometry and transmission electron microcroscopy (TEM) to be an ionomer with domains of maleate ionic groups. With increasing ionic groups, the water absorbency and the dilute solution viscosity of the ionomer increase, whereas the oil absorbency decreases. The tensile strength and ultimate elongation of ionomers increase with ionic group content and are higher than those of the original SBS without using any ionic plasticizer, which is usually used with the sulfonated ionomer. The ionomers with 1.2–1.7 mmol ionic groups/g exhibit optimum mechanical properties and behave as thermoplastic elastomers. The ionomer can be used as a compatibilizer for the blends of SBS with oil resistant chlorohydrin rubber (CHR). Addition of 3 wt% ionomer to the blend can increase the tensile strength and ultimate elongation of the blend optimally. The compatibility of the blends enhanced by adding the ionomer was shown by scanning electron microscopy (SEM). The blend of equal weight of SBS and CHR compatibilized by the ionomer behaves as a toluene resistant thermoplastic elastomer.

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

1 Introduction

(Styrene-butadiene-styrene) triblock copolymer (SBS) is a kind of thermoplastic elastomer which behaves like a crosslinked elastomer at ambient temperature and can be processed at elevated temperature as thermoplastics, due to the existence of physical crosslinks, formed by the glassy domains of polystyrene blocks. Since it is of a nonpolar nature, its modification to form thermoplastic elastomer with polar groups has attracted interest, in order to widen its uses. Ionomer is a kind of polymer containing less than 10 mol% ionic groups and shows characteristic properties due to the presence of ionic domains. Ionomers of sulfonated rubbers, such as ethylene-propylene-diene copolymer, butyl rubber and styrene-butadiene rubber with high styrene content, are thermoplastic elastomers with ionic domains as physical crosslinks in the presence of an ionic plasticizer (1–5). Weiss et al. (6) prepared ionomer based on hydrogenated SBS (SEBS) by reaction with acetyl sulfate followed by neutralization of the sulfonated product. The SEBS ionomers exhibit improved thermal–oxidative stability. Maleated EPDM rubber has not been exploited as a potential ionomer for a long time. Datta et al. (7) obtained maleated EPDM ionomer by mixing zinc oxide with maleated EPDM containing 1% dicarboxylic acid content made by Uniroyal Chem. Co. and studied the effect of zinc stearate. Ionomers of maleated and sulfonated SEBS were prepared by De et al. (8, 9) through sulfonation of maleated SEBS, a Kraton product with dicarboxylic acid content below 2 wt%, and

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Address correspondence to: Hong-Quan Xie, Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: xiehongquan88@126.com

neutralization by different metal acetates. Xie et al. (10) 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 the reaction extent is not high. Recently Antony and De gave a review about ionic thermoplastic elastomers (11). Udipi (12) epoxidized SBS by peracid in solution. Studies related to the addition of nucleophilic reagents, such as acid, amine and alcohol onto epoxidized polydiene were performed by Soutif et al. (13), Jayawardena et al. (14) and Derouet et al. (15), respectively. Soutif et al. (13) 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. (15) modified epoxidized 1,4-polyisoprene via ring-opening reaction with alcohol using cerium ammonium nitrate as catalyst. Recently Xie et al. (16) synthesized quaternary ammonium ionomer of SBS via ring-opening reaction of epoxidized SBS with triethylamine hydrochloride.

This paper deals with the synthesis conditions for the preparation of maleated SBS ionomer via first epoxidation of SBS in solution by peracid in the presence of phase transfer catalyst, followed by ring-opening reaction of epoxidized SBS with potassium hydrogen maleate without nitrogen atmosphere. The product containing potassium maleate groups is different in structure from that obtained by the reaction of SBS with maleic anhydride in the presence of benzoyl peroxide, which contains succinate groups. Its characterization with FTIR and TEM, as well as its water absorbency, oil absorbency, dilute solution properties and mechanical properties were studied. Behavior of the ionomer as a compatibilizer in blending of oil resistant chlorohydrin rubber with SBS via ion-dipole interaction was also studied.

2 Experimental

2.1 Materials

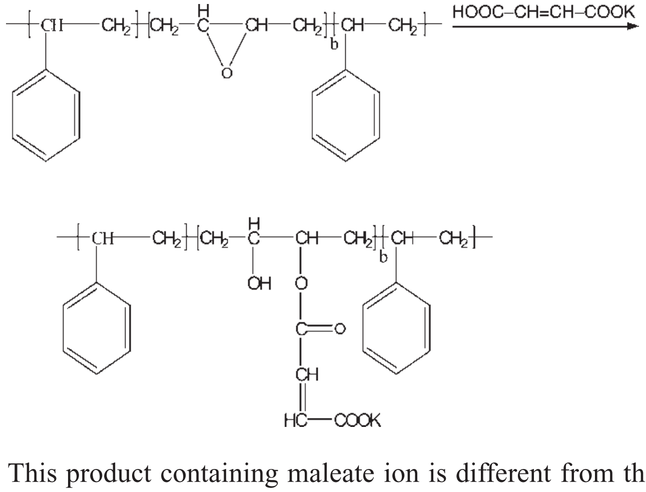
SBS of YH791 type is a product made by Yue-Yang Synthetic Rubber Factory in China with molecular weight about 100,000 and polystyrene blocks content of 30%. Chlorohydrin rubber H55 was supplied by Wuhan Synthetic Materials Factory. Lead acetates, acetone, formic acid (85%), hydrogen peroxide (30%), maleic anhydride, cyclohexane, tetraethyl ammonium bromide (TEAB), 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 (36%) and KOH were analytical reagents. Potassium hydrogen maleate (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 hour at room temperature.

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

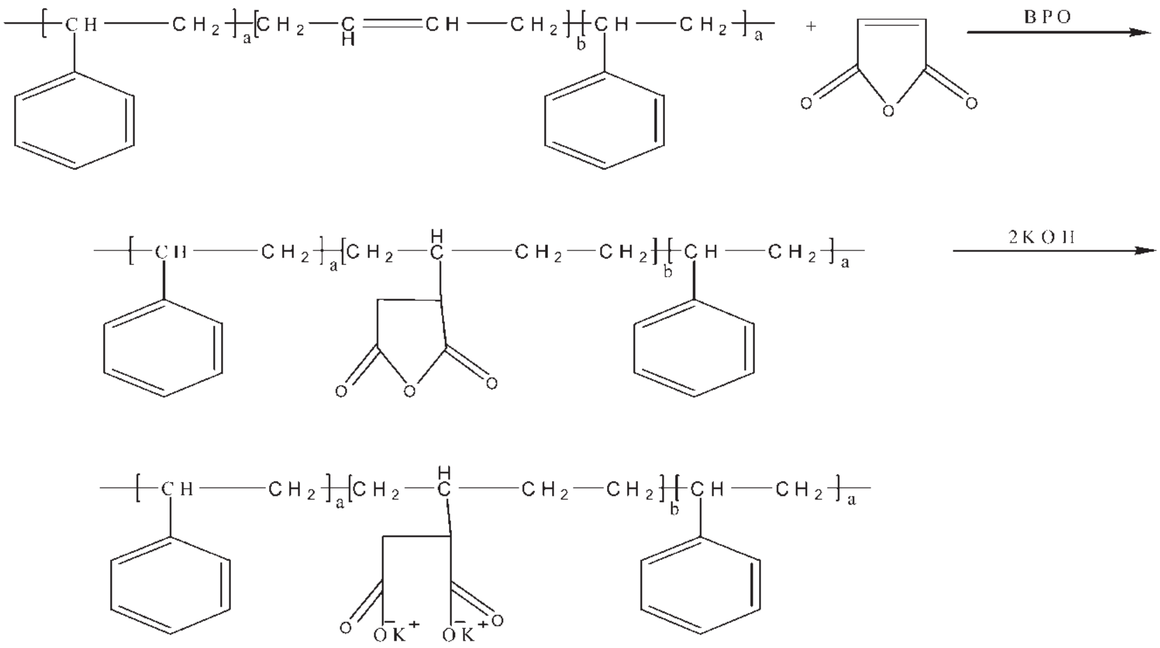
Epoxidation of SBS was carried out via reaction of SBS in cyclohexane solution at concentration of 11 g/100 mL with performic acid formed *in situ* by HCOOH and 30% aqueous H_2O_2 solution at 70°C for 2 h, using 5 wt% PEG 600/SBS as a phase transfer catalyst. The molar ratio of H_2O_2/HCOOH was 1. The 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.

2.3 Ring-opening Reaction of Epoxidized SBS with Potassium Hydrogen Maleate to Prepare Potassium Maleated Ionomer of SBS

The ionomer was made by the ring-opening reaction of epoxy groups in the epoxidized SBS (ESBS) with potassium hydrogen maleate as follows: ESBS was first dissolved in toluene with stirring to form a solution with concentration of 12 g/100 mL, into which were added 5 wt% dimethylaniline based on ESBS as ring-opening reaction catalyst and 5 wt% TEAB based on ESBS as a phase transfer catalyst. An aqueous solution of PHM and DPM, according to a molar ratio of PHM/epoxy group at 1.6 and a weight ratio of DPM/PHM at 40%, was then added with vigorous stirring at 70°C for 6 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, 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 SBS 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 C=C double bond in the former product.

2.4 Chemical Analysis

Epoxy group in the ESBS was determined by the HCl-acetone method (17) 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 were 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.

2.5 Characterization

FTIR spectrum of the maleated SBS 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 SBS ionomer was obtained by a Phillips CM300 transmission electron microscope (Netherland), after the potassium ionomer was treated with lead acetate solution, followed by washing with water and drying. Scanning electron micrographs were taken by JSM–5610 scanning 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, lubricant oil, toluene 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

Dilute solution viscosity (η_r/C) of the ionomers in toluene at about 0.5 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.

2.8 Mechanical Properties of the Ionomer

The ionomer was mixed with 1% antioxidant 264 on a hot roll and then hot pressed at 160°C. 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.

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

Blending of SBS with CHR in 50/50 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 Ring-Opening Reaction of Epoxy Groups in the Epoxidized SBS (ESBS) with Potassium Hydrogen Maleate*

The solubility of potassium hydrogen maleate (PHM) in water is much higher than that of sodium hydrogen maleate. Hence, the potassium hydrogen maleate was used in the ring-opening reaction with ESBS.

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 PHM, 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.

The addition of dipotassium maleate (DPM) seems very important to increase the epoxy conversion. Figure 1 shows that in the absence of dipotassium maleate the conversion is as low as about 26%. With an increasing amount of dipotassium maleate, the epoxy conversion increases. However, over 40% DPM/PHM, epoxy conversion levels off. Since DPM is more alkaline than PHM, the reaction seems to be better carried out in a comparatively more alkaline medium than that containing PHM only.

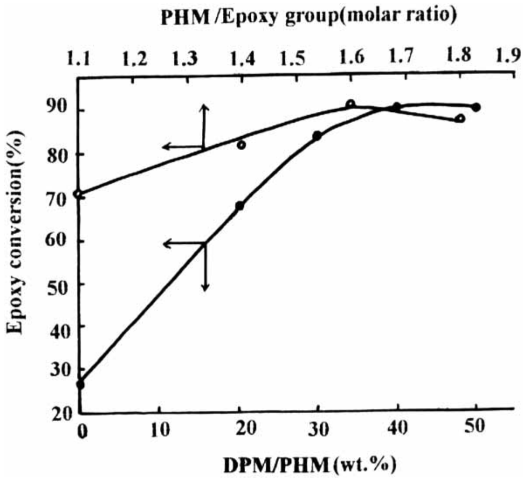


Fig. 1. Effects of dipotassium maleate amount and molar ratio of potassium hydrogen maleate/epoxy group on the epoxy conversion.

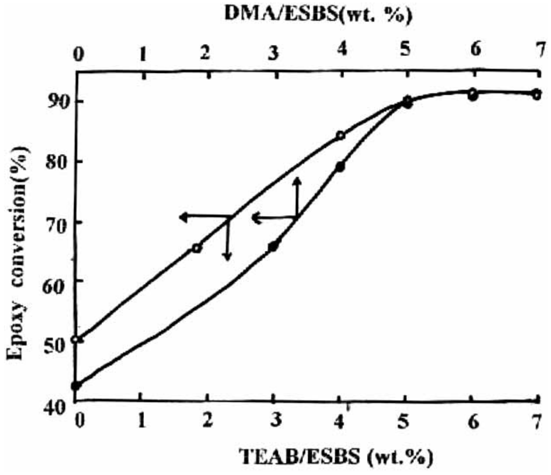


Fig. 2. Effects of N,N-dimethyl aniline amount and tetraethyl ammonium bromide amount on the epoxy conversion.

The effect of the molar ratio of potassium hydrogen maleate (PHM)/epoxy group on epoxy conversion is also shown in Figure 1. With increasing the molar ratio, the conversion increases till to molar ratio of 1.6. Excess reagent seems necessary to obtain high conversion, because the ring-opening reaction was carried out in heterogeneous phases.

Since the reaction is carried out between the toluene solution of ESBS and aqueous solution of PHM, it seems necessary to use a phase transfer catalyst. Tetraethyl ammonium bromide (TEAB) was used as a phase transfer catalyst. Figure 2 shows that without TEAB, the epoxy conversion is 50%, even in the presence of DPM and ring-opening catalyst. With increasing the TEAB amount, the epoxy conversion increases, evidently till to 5% TEAB based on ESBS and then levels off.

The ring-opening catalyst for reaction of epoxy group with carboxylic acid, such as N,N-dimethyl aniline (DMA), was also tested. It is also shown in Figure 2 that in the absence of DMA the conversion of epoxy groups is only 42% even in the presence of DPM and TEAB. It increases with DMA amount till to 5% DMA and then levels off. The conversion of epoxy groups was raised almost twice, when 5% dimethylaniline was added as catalyst.

The conversion of epoxy group increases with time, more rapidly before 5 h, and then gradually, as shown in Figure 3.

Figure 3 also indicates that the conversion of epoxy groups increases with reaction temperature from 55°C to 70°C. 70°C is the optimum reaction temperature for the ring-opening reaction of epoxy groups to form maleate ion groups. Over 70°C, the conversion decreases.

The concentration of ESBS affects the epoxy conversion evidently, as shown in Figure 4. In order to obtain high conversion about 95%, 15% ESBS solution may be used. Over that concentration, the solution is difficult to be stirred.

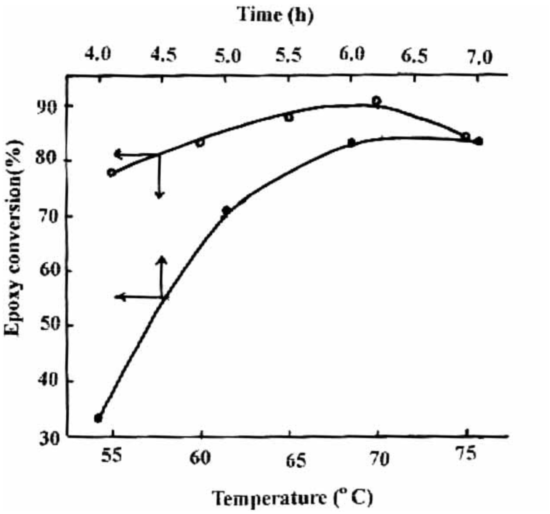


Fig. 3. Effect of reaction time (at 60°C) and reaction temperature on epoxy conversion.

3.2 Characterization of the Potassium Maleated Ionomer of SBS

The FTIR spectrum (Figure 5) of the potassium maleate groups containing SBS showed that absorption peaks at 810, 880 cm^{-1} for the epoxy groups nearly disappeared. There exist absorption peaks at 910, 968 and 731 cm^{-1} for the double bonds of polybutadiene segments and those at 699, 1449, 1311 cm^{-1} for the phenyl groups. The broad absorption peak at about 3450 cm^{-1} exists for OH group, which was formed simultaneously during ring-opening reaction of epoxy groups with potassium hydrogen maleate. 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 of COO^- group. Thus the FTIR spectrum shows the functional groups of the maleate ionomer of SBS.

Transmission electron microphotograph (Figure 6) shows the black spots in the specimen of potassium maleated SBS 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 ionic domains, the latter appear as dark spots. The diameters of the ionic domains are in the range of 3 nm to 8 nm. Thus, the TEM demonstrates the product obtained to be an ionomer, which also seems to be a nanocomposite in molecular level.

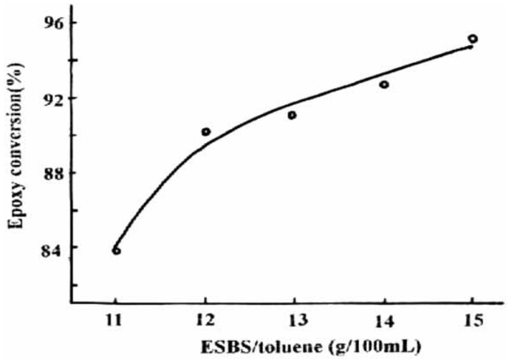


Fig. 4. Effect of ESBS concentration on epoxy conversion.

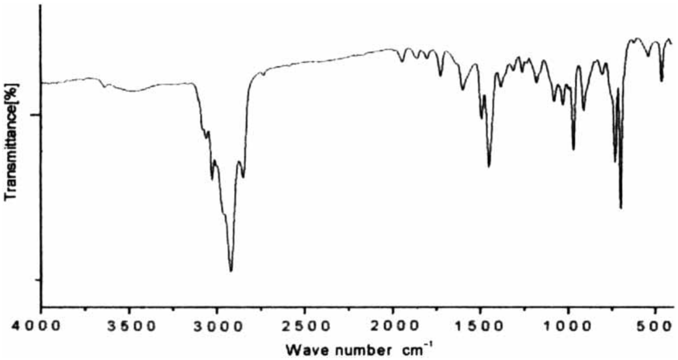


Fig. 5. FTIR spectrum of the potassium maleated ionomer of SBS.

3.3 Some Properties of the Potassium Maleated Ionomer of SBS

The ionomer can absorb water, because it contains the hydrophilic potassium maleate ion group. Table 1 indicates that with increasing potassium maleate ion groups, water absorbency increases.

Table 1 also shows that the ionomer offers some oil resistant properties. SBS is completely dissolved in kerosene oil for 48 h at room temperature, whereas the SBS ionomers containing more than 0.5 mmole ionic groups/g do not dissolve, but absorb oil. The oil absorbency 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 toluene increases with increasing ionic groups, as also shown in

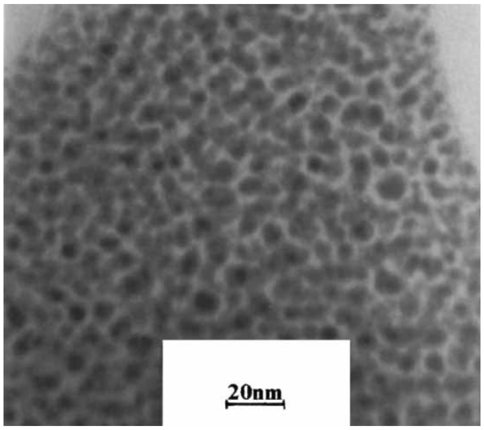


Fig. 6. TEM microphotograph the lead maleated ionomer of SBS.

Table 1. Effect of ionic group content on water absorbency, oil absorbency and dilute solution viscosity of the maleated ionomer of SBS

Maleated groups (mmole/g)	Water absorbency (%)	Kerosene absorbency (%)	Lubricant oil absorbency (%)	η_r/C (mL/g)
0.535	6.99	739	52.2	221
1.23	20.8	408	36.6	228
1.69	45.5	75.0	15.6	234
2.28	79.2	45.2	2.39	272

Table 1. It increases more sharply over 1.7 mmole ionic groups/g. This phenomenon can be explained by the fact that the more the ionic groups, the more the association between the ions of ionomer macromolecules, resulting in higher resistance to flow or higher viscosity.

3.4 Mechanical Properties of the Potassium Maleated SBS Ionomers

Table 2 indicates that the ionomer possesses better tensile strength and ultimate elongation than those of the original SBS. This fact can be explained by the additional physical crosslinkage due to the ionic domains beside the physical crosslinks contributed by the glassy domains of the polystyrene blocks of SBS. It is interesting to note that this kind of ionomer can be processed smoothly and shows good mechanical properties without using any ionic plasticlizer, which is usually used with the sulfonated ionomer. This fact is probably attributed to the weaker interaction between the carboxylate groups of the ionomer molecules than that between the sulfonate groups. With increasing ionic content, both the tensile strength and ultimate elongation of the ionomer increase, due to the increased number of ionic domains formed in the ionomers with higher potassium maleate content. However, with increasing ionic groups exceeding 1.7 mmole/g, the tensile strength and ultimate elongation of the ionomer decrease. This fact can be interpretated as the excess physical crosslinks formed by too much or too large ionic domains.

Table 2. Effect of ionic group content on mechanical properties[a] of the ionomer

Ionic group content (mmol/g)	TS (MPa)	UE (%)	PS (%)
0	9.13	414	16
0.535	14.9	1280	20
1.23	16.8	1320	20
1.69	16.1	1150	18
2.28	15.2	800	22

[a] TS represents tensile strength, UE ultimate elongation and PS permanent set.

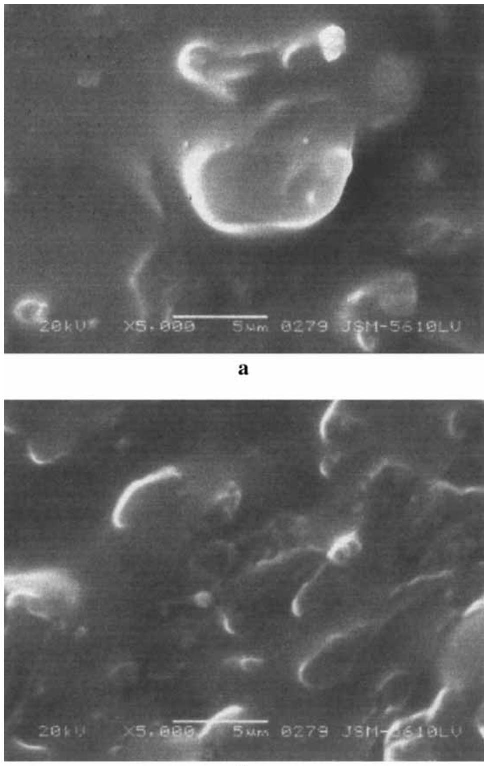
Table 3. Effect of amount of the ionomer added on the mechanical properties of the SBS/CHR (50/50 weight ratio) blends

Amount of ionomer[a] (wt%)	TS (MPa)	UE (%)	PS (%)
0	8.94	840	18
1	9.92	950	18
2	10.5	1060	20
3	11.2	1070	20
4	10.4	966	18
5	10.3	970	18

[a] The ionic group content of the ionomer used was 2.28 mmol/g.

3.5 Behavior of the Potassium Maleated Ionomer as a Compatibilizer for SBS/CHR Blends

Hara et al. (18) indicated the miscibility enhancement via ion-dipole interaction between polystyrene ionomer and poly(alkylene oxide). Here the ionomer was tested as a compatibilizer for blending thermoplastic elastomer SBS and oil resistant chlorohydrin rubber (CHR) so as to utilize the ion-dipole interaction. Table 3 shows the effect of ionomer amount on the mechanical properties of the blends with weight ratio of SBS/CHR at 50/50. Both the tensile strength and ultimate



a

b

Fig. 7. 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 5000x.

elongation of the blend increase with 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-dipole interaction between potassium ion of the ionomer and ether linkage of CHR on the one side and to the miscibility between SBS phase and SBS part of the ionomer on the other side, thus enhancing the compatibility between SBS and CHR. 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 and the particles in the former seems smaller with edges less sharper than that of the latter, as shown in Figure 7.

The SBS/CHR (1/1 weight ratio) blend with 3% ionomer as compatibilizer behaves as an oil resistant thermoplastic elastomer with toluene absorbency of 170% for 48 h at room temperature, whereas that without ionomer swelled and was partially dissolved in toluene.

4 Conclusions

The maleated ionomer can be obtained by ring-opening reaction of epoxidized SBS with an aqueous solution of potassium hydrogen maleate. The optimum conditions are: DPM/PHM = 40 wt%, PHM/epoxy group = 1.6 molar ratio, DMA/ESBS = 5 wt%, TEAB/ESBS = 5 wt%, ESBS/toluene = 14 g/100 mL at 70°C for 6 h. Characterization by FTIR and TEM showed that the product was really an ionomer with maleate ionic groups domains. With increasing the hydrophilic ionic groups, the water absorbency of the ionomer increases, whereas the oil absorbency decreases. The dilute solution viscosity of the ionomer increases with increasing ionic group content, due to the association of the ionic groups between the ionomer macromolecules in the nonpolar solvent. The ionomer exhibits improved mechanical properties than SBS in the absence of any ionic plasticizer, because of the formation of ionic domains. The tensile strength and ultimate elongation of the ionomer increases with increasing the ionic group up to 1.7 mmol/g. It can be used as a compatibilizer for the blends of SBS and CHR via ion-dipole interaction. 3 wt% ionomer based on the blend can increase the tensile strength and ultimate elongation of the blend optimally. The compatibility of the blends enhanced by adding the ionomer was shown by scanning electron microscopy (SEM). The blend of equal weight of SBS and CHR compatibilized by the ionomer behaves as an oil resistant thermoplastic elastomer.

5 Acknowledgement

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