

Novel Method for Preparation of Quaternary Ammonium Ionomer from Epoxidized Styrene–Butadiene–Styrene Triblock Copolymer and Its Use as Compatibilizer for Blending of Styrene–Butadiene–Styrene and Chlorosulfonated Polyethylene

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ABSTRACT: A novel method for the preparation of a quaternary ammonium ionomer of styrene–butadiene–styrene triblock copolymer (SBS) was developed by a ring-opening reaction of epoxidized SBS with triethylamine hydrochloride in the presence of a phase transfer catalyst. The optimum conditions were studied. The ionomer was characterized by quantitative analysis, IR spectroscopy, and ¹H-NMR spectroscopy. Its water absorbency, oil absorbency, dilute solution viscosity, and use as a compatibilizer for the blending of SBS and chlorosulfonated polyethylene (CSPE) were investigated. The results showed that, under optimum conditions, the epoxy groups can be completely converted to the quaternary ammonium groups. The IR spectrum did not exhibit the absorption peak for quaternary ammonium groups, whereas the ¹H-NMR spectrum and titration method demonstrated it. With increasing ionic group con-

centration, the water absorbency of the ionomer increased whereas its oil absorbency decreased. These indicated the amphiphilic character of the SBS ionomer. The dilute solution viscosity of the ionomer in toluene/methanol (9/1) solvent increased with increasing quaternary ammonium group content. The ionomer was used as a compatibilizer for the blends of SBS and CSPE. The addition of a small amount of the ionomer to the blend enhanced the mechanical properties of the blends: 2 wt % ionomer based on the blend increased the tensile strength and ultimate elongation of the blend nearly 2 times. The blends of equal parts SBS and CSPE behaved as oil-resistant thermoplastic elastomers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1975–1980, 2006

Key words: styrene–butadiene–styrene; ionomer; quaternary ammonium salt; compatibilization; blends

INTRODUCTION

The styrene–butadiene–styrene triblock copolymer (SBS) is an important thermoplastic elastomer with a multiphase structure, and it has been used in many applications. Because it has a nonpolar nature, recent research about its modification to contain polar groups has attracted much interest in order to widen its uses. An ionomer is a kind of polymer containing less than 10% ionic groups, and it shows characteristic properties that are due to the presence of ionic domains. Ionomers made from SBS and hydrogenated SBS (SEBS), such as maleated and sulfonated SEBS¹ and maleated SBS neutralized with metallic ions,²

have been reported recently. Very few reports have been concerned with the quaternary ammonium ionomers.^{3–6} Reusche et al.³ obtained a quaternary ammonium ionomer from styrene–isobutylene–styrene block copolymers by using the reaction of the sulfonated block copolymer with quaternary ammonium hydroxide. Huang et al.⁴ prepared a quaternary ammonium ionomer from chloroalkyl-containing polysiloxane with tertiary amine. Ma et al.⁵ obtained the quaternary ammonium ionomer of methylstyrene–isobutylene diblock copolymer by bromination of the copolymer, followed by a reaction with triethylamine. Buzdugen et al. synthesized a quaternary ammonium ionomer from SBS via bromination of SBS with bromine, followed by a reaction with tertiary amine.⁶ The ionomer was only characterized by IR spectroscopy. However, Silverstein et al.⁷ indicated that the quaternary ammonium group has no characteristic absorption peak in the IR spectrum. Until now, no other

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research work about a quaternary ammonium ionomer from SBS has appeared in the literature.

This article deals with a novel method for the preparation of an amphiphilic quaternary ammonium ionomer of SBS via epoxidation of SBS, followed by a ring-opening reaction with a tertiary amine hydrochloride and its characterization with quaternary ammonium group titration and IR and $^1\text{H-NMR}$ spectroscopies. Some properties and its application as a compatibilizer for the blending of SBS and chlorosulfonated polyethylene (CSPE) were also studied. The aim of this work was to prepare an amphiphilic SBS with an ionic moiety in order to provide antielectrostatic and polar properties to SBS to make it applicable for fabric coatings and as an adhesive between polar and nonpolar materials, as well as a compatibilizer for blending of polar and nonpolar polymers.

EXPERIMENTAL

Materials

A YH791-type SBS containing 30 wt % polystyrene blocks was supplied by Yueyang Synthetic Rubber Factory. Triethylamine, acetone, formic acid (85%), hydrogen peroxide (30%), cyclohexane, tetraethyl ammonium bromide (TEAB), and ethanol were chemically pure. Antioxidant 264 (2,6-di-*tert*-butyl-4-meth-

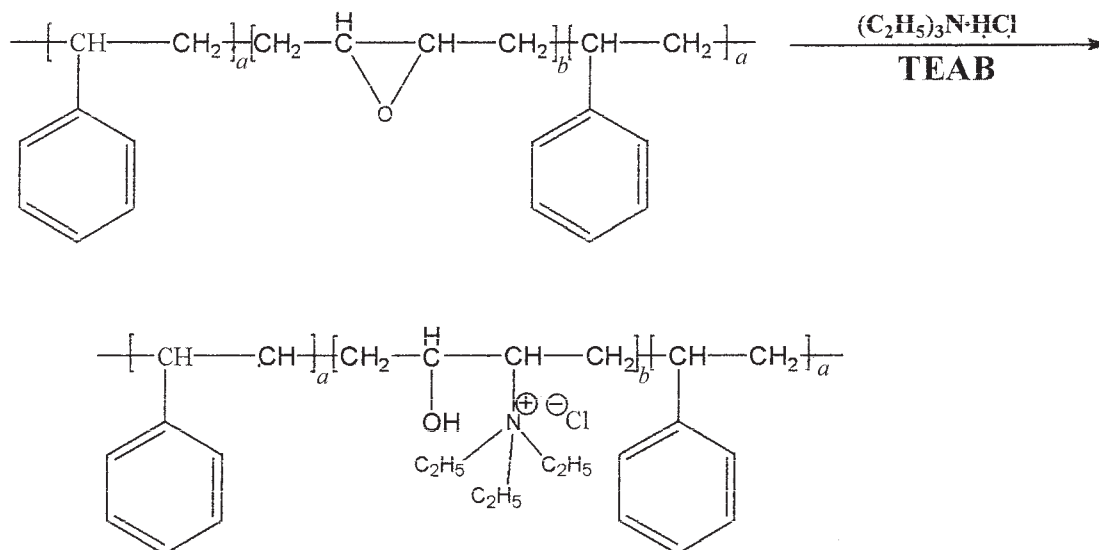
ylphenol) was an industrial product. Hydrochloric acid and KOH were used as analytical reagents.

Epoxidation of SBS

Epoxidation of SBS was carried out via a reaction of SBS in cyclohexane solution (SBS concentration = 13 g/100 mL) with HCOOH and 30% aqueous H_2O_2 solution at 70°C for 2 h, using 1 wt % poly(ethylene glycol)/SBS 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 ethanol, followed by drying in a vacuum dryer at 60°C .

Preparation of quaternary ammonium ionomer of SBS

The ionomer was made by the ring-opening reaction of epoxy groups in the epoxidized SBS (ESBS) with triethylamine hydrochloride salt (TEAS) as follows: ESBS was first dissolved in cyclohexane (ESBS concentration = 15 g/100 mL), into which was added 3 wt % TEAB/ESBS as a phase transfer catalyst. An aqueous solution of TEAS was then added with vigorous stirring at 70°C for 5 h with a 1.2 molar ratio of TEAS/epoxy group. The reaction was terminated by adding a small amount of acetone solution containing antioxidant 264. The mixture was washed with distilled water to neutrality and then precipitated by ethanol, followed by drying in a vacuum dryer at 50°C .



Chemical analysis and characterization

The epoxy group in the ESBS was determined by the HCl-acetone method.⁸ Briefly, about a 1-g sample was accurately weighed into an iodometric titration flask and 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, 3 drops of phenolphthalein indicator were added and the solution was titrated with standard alcoholic KOH solution to a pink color. The epoxy value was determined according to the following equation:

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

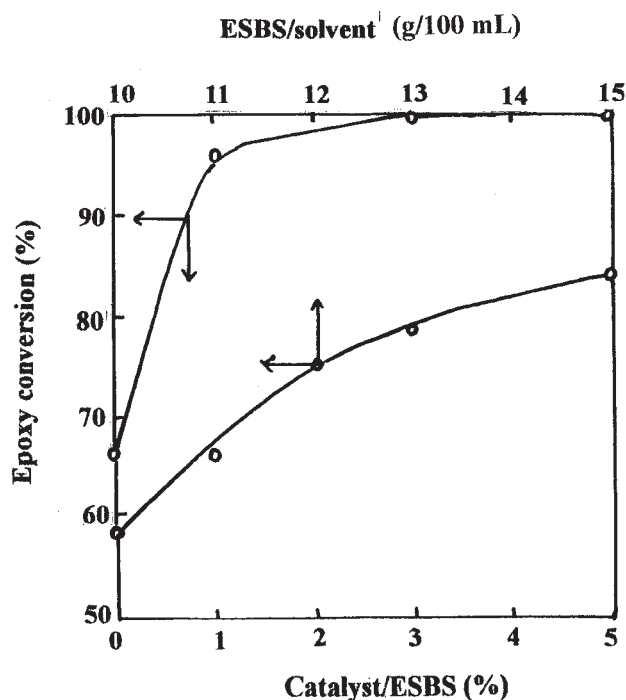


Figure 1 The effects of the amount of phase transfer catalyst and ESBS concentration on the epoxy conversion.

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

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

The quaternary ammonium groups were determined by HClO_4 titration.⁸ An approximate 0.2-g sample was accurately weighed into a conical flask, and 10 mL of toluene were added to dissolve it. Then, 10 mL of glacial acetic acid/acetic anhydride (1/9) and 10 mL of glacial acetic acid were added and the reaction was carried out at room temperature for 60 min. After cooling, the mixture was titrated with 0.01M HClO_4 -glacial acetic acid with 2 drops of crystal violet solution as an indicator. The HClO_4 -glacial acetic acid solution was standardized with potassium hydrogen phthalate. The quaternary ammonium group content was derived from the following equation:

$$\begin{aligned} \text{quaternary ammonium group content (mmol/g)} \\ = (V - V_0)N/W \end{aligned}$$

where V and V_0 are the volume (mL) of HClO_4 -glacial acetic acid solution used in the titration of the sample

and blank, respectively; N is the normality of the HClO_4 -glacial acetic acid solution; and W is the weight of the sample.

The IR spectra were taken with an Equinox 55 type FTIR spectrophotometer. The $^1\text{H-NMR}$ spectra were obtained with a Varian Mercury Plus 300-MHz NMR spectrometer using CDCl_3 as a solvent and tetramethyl silane as an internal standard.

Water or oil absorbency was determined by immersing an accurately weighed sample (W_b) in water or diesel oil 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), according to the following equation:

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

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

RESULTS AND DISCUSSION

Synthesis conditions for quaternary ammonium ionomer of SBS

Because the reaction was carried out in a mixture of cyclohexane and water phases, it is necessary to use a phase transfer catalyst, such as TEAB, to increase the conversion of epoxy groups. Figure 1 shows that, in the absence of a phase transfer catalyst, the conversion of epoxy groups reaches only 66%, even with a reaction time of 6 h. When 1 wt % TEAB based on ESBS is used, the conversion can reach 95% at 5 h. When 3 wt % of the phase transfer catalyst is used, the ring-opening reaction is completed in 5 h.

Figure 1 also indicates that increasing the ESBS concentration causes the conversion of epoxy groups into quaternary ammonium groups to increase quickly below 11 g/100 mL and then gradually. However, the reaction solution becomes too viscous and difficult to stir when the ESBS concentration is over 15 g/100 mL. Hence, the optimum ESBS concentration is 15 g/100 mL.

With an increasing molar ratio of TEAS/epoxy group, the conversion increases, as shown in Table I. At a TEAS/epoxy group molar ratio of 1.0 the conversion reaches above 90%, whereas at a molar ratio of 1.2 the ring-opening reaction is complete.

Figure 2 shows that the reaction temperature is very important in determining the conversion of epoxy groups. The reaction rate is lower below 60°C, but over 65°C the reaction rate increases rapidly. The optimum temperature is 70°C for obtaining high conver-

TABLE I
Effect of Molar Ratio of TEAS/Epoxy Group on
Conversion of Epoxy Group in ESBS to Form Ionomer

TEAS/epoxy (molar ratio)	Epoxy in ESBS (%)	Epoxy in product (%)	Conversion (%)
1.0	7.39	0.52	93.0
1.1	7.39	0.32	95.7
1.2	7.39	0	100

ESBS concentration = 15 g/100 mL; catalyst/ESBS = 3 wt %; 70°C; 5 h.

sion. The conversion decreases at 75°C, probably because of some side reactions

The conversion increases rapidly within 1 h and then gradually up to 5 h, which is shown in Figure 2. In order to obtain higher conversion of epoxy groups, a long reaction time seems necessary.

The conversion of the epoxy group in ESBS can reach 100% with the following optimum conditions: an ESBS concentration of 150 g/L, a molar ratio of triethylamine hydrochloride/epoxy group of 1.2, and a weight ratio of TEAB/ESBS of 3% at 70°C for 5 h.

Characterization of quaternary ammonium ionomer of SBS

The purified quaternary ammonium ionomer was characterized by determination of the quaternary ammonium groups using the titration with perchloric acid method.⁸ The results showed that the amount

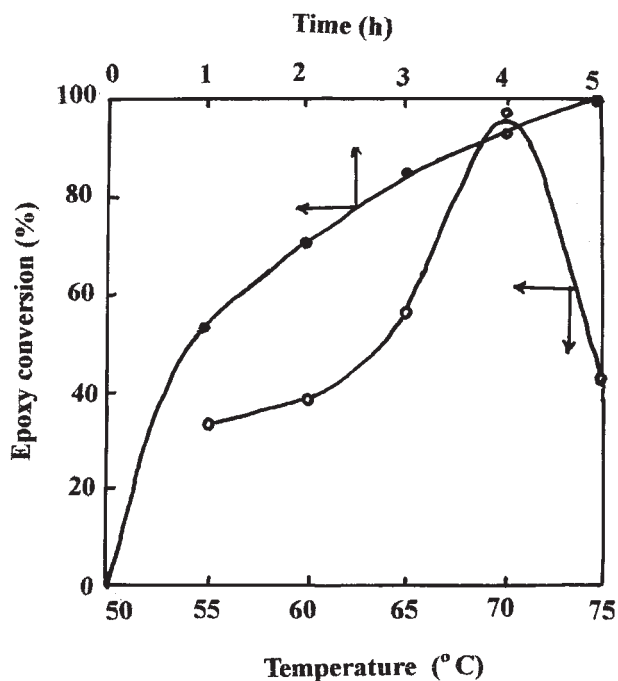


Figure 2 The effects of the reaction temperature and time on the epoxy conversion.

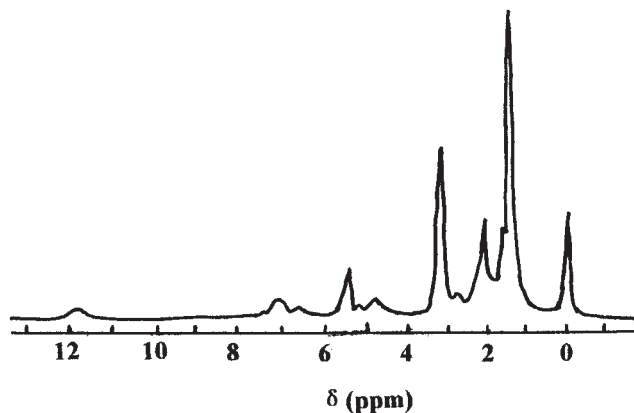


Figure 3 The ¹H-NMR spectrum of the quaternary ammonium ionomer of SBS.

epoxy groups converted was almost equal to the quaternary ammonium group content. For example, the sample obtained by 100% conversion of a 12.12 wt % epoxy group of ESBS was determined by perchloric acid titration to contain 2.88 mmol/g quaternary ammonium groups.

The FTIR spectrum of the quaternary ammonium groups containing SBS showed that absorption peaks at 810, 880, and 1265 cm^{-1} for the epoxy groups disappeared. Absorption peaks at 967, 914, and 759 cm^{-1} occur for the double bonds of the polybutadiene block and those at 699, 1449, and 1311 cm^{-1} exist for the phenyl groups. The broad absorption peak at 3435 cm^{-1} indicates the OH group, which was formed during the ring-opening reaction of epoxy groups with triethylamine hydrochloride. It is known⁷ that no special absorption peak for quaternary ammonium groups appears in the IR spectrum.

Figure 3 shows the ¹H-NMR spectrum of the quaternary ammonium ionomer of SBS, in which the proton peaks at 1.45, 1.65, 2.05, 3.13, 4.67, 4.98, 5.41, and 6.5–7.3 ppm indicate CH_3 , CH_2 , CH , quaternary ammonium groups, OH groups, 1,2-unsaturated olefin groups, 1,4-unsaturated olefin groups, and phenyl groups, respectively. The ¹H-NMR spectrum demonstrates the presence of quaternary ammonium groups in the product.

Properties of quaternary ammonium ionomer of SBS

The ionomer can absorb water, because it contains the hydrophilic quaternary ammonium ion group. Table II indicates that increasing the quaternary ammonium ion groups causes the water absorbency to increase, more obviously over 1.0 mmol/g ionic groups.

Table II also shows that the ionomer offers some oil-resistant properties. SBS is completely dissolved in diesel oil for 48 h at room temperature, whereas the

TABLE II
Water Absorbency and Oil Absorbency of Quaternary Ammonium Ionomer of SBS

Quaternary ammonium groups (mmol/g)	Water absorbency (%)	Oil absorbency (%)
0	0.2	Soluble
0.97	15.3	Partially soluble
1.44	58.0	208.9
1.76	61.2	189.4
2.34	89.7	128.7
2.40	93.0	—
2.85	97.3	102.8

SBS ionomer containing more than 1.5 mmol/g quaternary ammonium groups absorbs oil but does not dissolve. The oil absorbency decreases when increasing the quaternary ammonium groups. This fact is attributed to the association of the ionic groups in the nonpolar oil, resulting in oil resistance.

The η_r/C of the ionomers in a mixed solvent of toluene/methanol (9/1) increases with increasing quaternary ammonium groups, as shown in Figure 4. It increases more sharply over 2.0 mmol/g. This phenomenon can be explained by the fact that the more quaternary ammonium groups there are, the more the association between the macromolecules of the ionomer, resulting in higher resistance to flow or higher viscosity.

Behavior of quaternary ammonium ionomer of SBS as a compatibilizer for blending SBS with CSPE

The ionomer was tested as a compatibilizer for blending nonpolar SBS and polar oil-resistant CSPE. Table III

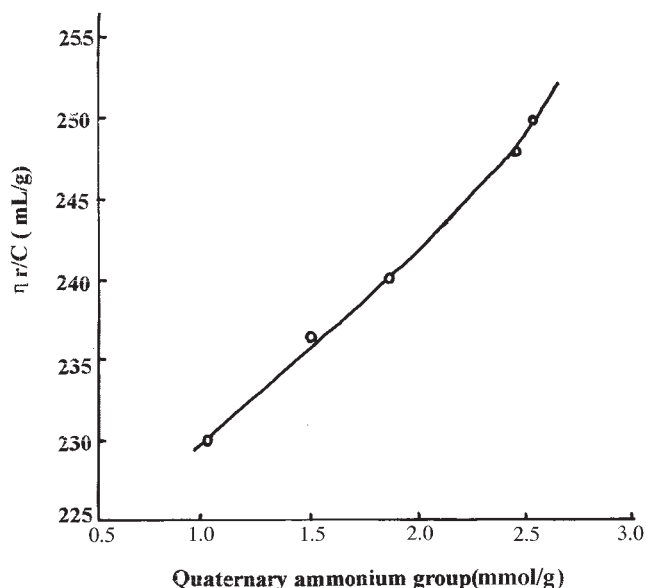


Figure 4 The relationship between the dilute solution viscosity (η_r/C) and the quaternary ammonium groups of the SBS ionomer.

TABLE III
Effect of Amount of Ionomer Added on Mechanical Properties of SBS/CSPE (50/50 w/w) Blend

Ionomer/blend (%)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	5.3	945	20
1	10.1	2860	25
2	12.1	1710	28
4	8.5	1330	20
5	7.3	960	18

shows the effect of the amount of ionomer on the mechanical properties of the blends with a 50/50 weight ratio of SBS/CSPE. Both the tensile strength and ultimate elongation of the blend increase with the addition of a small amount of the ionomer to the blend. Two percent of the ionomer based on the blend seems to be enough as a compatibilizer. This phenomenon may be attributed to the ionic-polar interaction between the quaternary ammonium ion of the ionomer and the polar SO_2Cl group of CSPE on the one hand and to the miscibility between the SBS component and the SBS part of the ionomer on the other hand, thus enhancing the interfacial adhesion and compatibility between SBS and CSPE. Four percent 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 the SBS phase, thereby decreasing the interfacial adhesion between the two phases and lowering the compatibilizing effect.

The surfaces of the broken sections of the blends with and without the ionomer used as a compatibilizer were observed with a Hitachi 530 scanning electron microscope, as shown in Figure 5(a,b). Note that the surface of the broken section of the blend with the compatibilizer seems smoother than that without the compatibilizer. This indicates that the two components in the blend with the compatibilizer are more compatible than those in the blend without the compatibilizer.

The blend behaves as an oil-resistant thermoplastic elastomer with a toluene absorbency of 24% for 48 h at room temperature.

CONCLUSIONS

A novel method for the preparation of a quaternary ammonium ionomer of SBS was developed by the ring-opening reaction of ESBS with triethylamine hydrochloride in the presence of a phase transfer catalyst. This new synthesis method for the quaternary ammonium ionomer of SBS is easy and efficient to carry out with 100% conversion of the epoxy groups. The optimum conditions are: ESBS concentration of 150 g/L, a molar ratio of triethylamine hydrochloride/epoxy group of 1.2, and a weight ratio of TEAB/

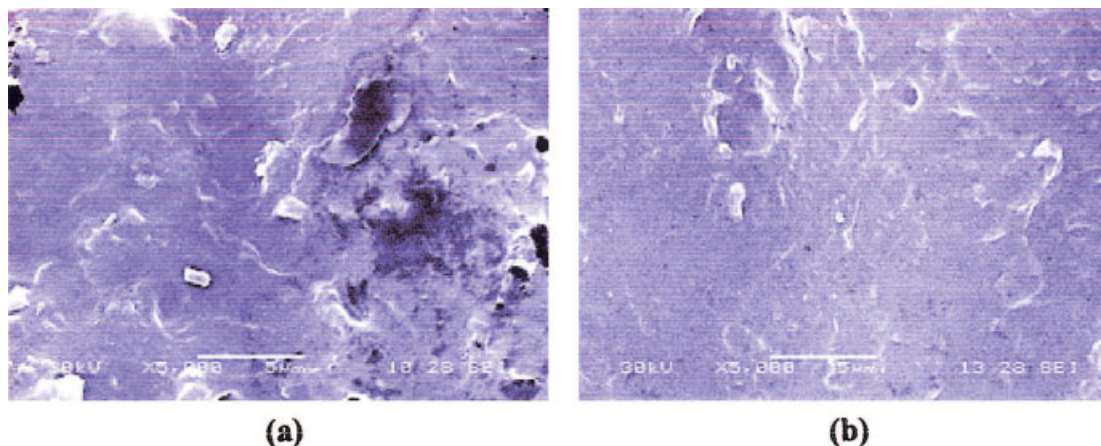


Figure 5 SEM micrographs of the broken section of the blend (a) without compatibilizer and (b) with 1% compatibilizer (original magnification $\times 5000$).

ESBS of 3% at 70°C for 5 h. The IR spectrum did not exhibit the absorption peak for quaternary ammonium groups, whereas the $^1\text{H-NMR}$ spectrum and titration method did demonstrate it. The quaternary ammonium ionomer of SBS can absorb some water and show oil resistance. With increasing ionic group content, the water absorbency of the ionomer increases whereas its oil absorbency decreases. The dilute solution viscosity of the ionomer increased with increasing quaternary ammonium groups content, because of the association of ionic groups between ionomer molecules. The ionomer can be used as a compatibilizer for the blends of SBS and CSPE. The addition of a small amount of the ionomer enhanced the mechanical properties of the blends. A 2% ionomer based on the blend increased the tensile strength and ultimate elongation of the blend nearly 2 times. A blend of equal parts of SBS and CSPE behaved as an oil-resistant thermoplastic elastomer.

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