

Amphiphilic Styrene–Butadiene–Styrene Triblock Copolymer Grafted with Polyoxyethylene

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ABSTRACT: A styrene–butadiene–styrene triblock copolymer (SBS) was grafted with polyoxyethylene via a ring-opening reaction of an epoxidized styrene–butadiene–styrene triblock copolymer (ESBS) with monocarboxylic-group-terminated methoxypoly(ethylene glycol) (CMPEG). The latter was prepared through the esterification of methoxypoly(ethylene glycol) with maleic anhydride. The optimum conditions for the preparation of the graft copolymer were studied. The graft copolymer was characterized with Fourier transform infrared spectrophotometry. Its water absorbency, oil absorbency, emulsifying property, phase-transfer catalysis property in the Williamson solid–liquid reaction, and use as a compatibilizer in the blending of SBS with oil-resistant chlorohydrin rubber (CHR) were also studied. The optimum conditions were a CMPEG/epoxy group molar ratio of 1.5, an *N,N*-dimethyl aniline/ESBS concentration of 5 wt %, and an ESBS concentration

of 12–14 g/100 mL at 75–80°C for 10 h. The polyoxyethylene content could reach 0.27 mmol/g. The graft copolymer absorbed a certain amount of water, fairly resisted kerosene, and possessed good emulsifying and phase-transfer catalysis properties, both of which were enhanced with increasing polyoxyethylene graft content. The graft copolymer could be used as a compatibilizer for a blend of SBS and CHR. A 3 wt % concentration of the graft copolymer based on a 50/50 blend could increase both the tensile strength and ultimate elongation of the blend about 1.7 times. The blend behaved like an oil-resistant thermoplastic elastomer. Scanning electron microscopy demonstrated the improved compatibility of the two components by the graft copolymer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 153–158, 2008

Key words: block copolymers; compatibility; elastomers; graft copolymers; phase transfer catalysts

INTRODUCTION

A styrene–butadiene–styrene triblock copolymer (SBS) is a type of nonpolar thermoplastic elastomer that cannot be compatible with or adherent to a polar substance. The modification of SBS is necessary to widen its applications. An amphiphilic polymer is a kind of polymer containing both hydrophilic and hydrophobic groups or segments. Block and graft copolymers containing hydrophilic polyoxyethylene (PEO) segments and hydrophobic segments have attracted much attention because not only are they amphiphilic but their PEO segments are also non-ionic and crystalline and can complex monovalent metallic ions.^{1–3} They have many uses, including polymeric surfactants, phase-transfer catalysts, solid polymer electrolytes, and compatibilizers in polymer blending. Graft copolymers with PEO side chains can be obtained by a macromer technique,^{4–6} a graft-

ing-on technique,⁷ and a grafting-from technique.⁸ A graft copolymer of polychloroprene with PEO side chains was prepared by Xie⁹ via the reaction of a sodium salt of poly(ethylene glycol) with polychloroprene rubber and used as a compatibilizer for blending a water-absorbing resin with an elastomer. Graft copolymers of SBS with PEO as grafts were synthesized by Giles et al.¹⁰ via the hydrogenation of an epoxidized styrene–butadiene–styrene triblock copolymer (ESBS) with LiAlH₄ to form a hydroxyl-group-containing SBS, and this was followed by a reaction with isocyanate-terminated methoxypoly(ethylene glycol); the conductivity of an ion-conducting material formed by the graft copolymer combined with LiCF₃SO₃ was studied.

This article deals with the preparation of an amphiphilic SBS containing PEO segments as grafts via a ring-opening reaction of ESBS with carboxylic-group-terminated methoxypoly(ethylene glycol) (CMPEG) in a way simpler than that previously reported.¹⁰ The product was characterized with Fourier transform infrared (FTIR) spectrophotometry, and its properties, such as its water absorbency, oil absorbency, and phase-transfer catalysis and emulsifying properties, and its use as a compatibilizer for a blend of SBS

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with oil-resistant chlorohydrin rubber (CHR) were studied.

EXPERIMENTAL

Materials

SBS (type YH791) was a product made by Yue-Yang Synthetic Rubber Factory (China) with a molecular weight of about 100,000 and a polystyrene block content of 30 wt %. Methoxypoly(ethylene glycol) with a molecular weight of 550 and poly(ethylene glycol) with a molecular weight of 600 were purchased from Aldrich Chemical Co. Acetone, formic acid (85%), hydrogen peroxide (30%), cyclohexane, toluene, *N,N*-dimethyl aniline (DMA), maleic anhydride, 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.

Epoxydation of SBS in the presence of a phase-transfer catalyst

The epoxydation of SBS was carried out via a reaction of SBS in a cyclohexane solution (SBS concentration = 11 g/100 mL) with performic acid formed from an 85% HCOOH and 30% aqueous H₂O₂ solution *in situ* with an H₂O₂/HCOOH molar ratio of 1 at 70°C for 4 h, with 1 wt % poly(ethylene glycol) 600 based on SBS as a phase-transfer catalyst. The product (ESBS) was precipitated and washed several times with ethanol, and this was followed by drying in a vacuum dryer at 60°C. ESBS was characterized by ¹H-NMR spectroscopy with a Varian Mercury Plus 300 NMR spectroscope, which showed peaks at 1.45, 2.05, 2.71, 2.95, 4.98, 5.41, and 6.5–7.3 ppm for protons of methylene, methane, *cis*-epoxy, *trans*-ep-

oxy, 1,2-double bonds, 1,4-double bonds, and phenyl groups.

Synthesis of CMPEG

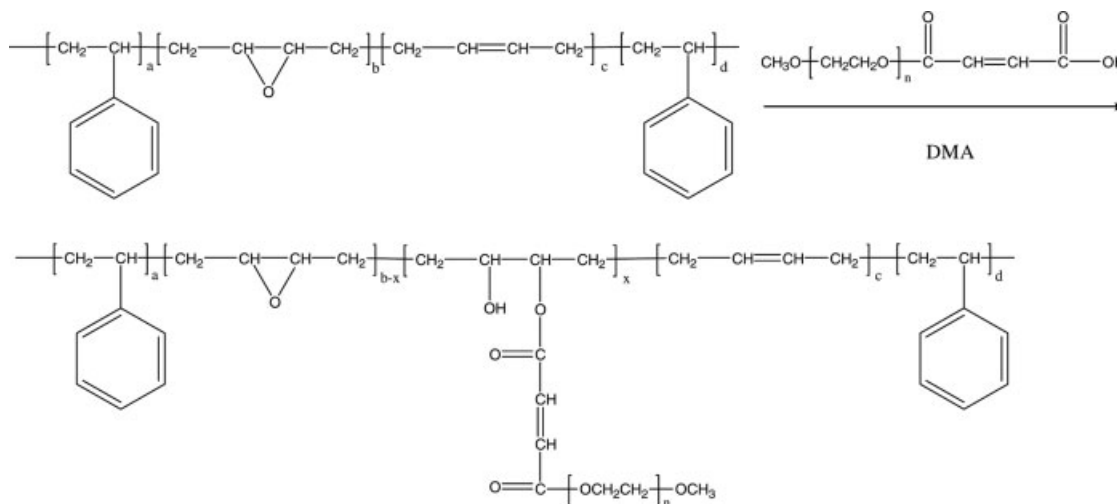
To a mixture of maleic anhydride and methoxypoly(ethylene glycol) in a molar ratio of 1/1 was added 5 wt % DMA, and the mixture was heated at 110°C for 10 h under a nitrogen atmosphere. The crude product was purified by extraction with ethyl ether to remove the unreacted maleic anhydride, methoxypoly(ethylene glycol), and DMA. The purified product was dried at 60°C in a vacuum dryer until a constant weight was obtained. The acid value of the product was determined with a 0.1M alcoholic KOH solution to be 1.58 mmol/g versus the theoretical value of 1.54 mmol/g.

Synthesis of a graft copolymer of SBS with PEO (SBS-g-PEO)

To a toluene solution of ESBS with 0.4–1.1 mmol of epoxy groups/g, at a concentration of 10 g/100 mL, 5 wt % DMA and a certain amount of CMPEG were added (Scheme 1). The mixture was heated with rigorous stirring at 70°C for 8 h. The product was washed with excess KOH solution to neutralize the unreacted carboxylic acid groups, and this was followed by precipitation into ethanol and then dissolution in toluene three times for purification. The precipitate was dried under an infrared lamp to hasten the evaporation of the solvent in the precipitate and then in a vacuum dryer at 60°C until a constant weight was obtained.

Chemical analysis

The epoxy group in ESBS was determined by the HCl-acetone method¹¹ as follows. An approximately



Scheme 1

TABLE I
Effects of the Amounts of DMA and CMPEG on the Epoxy Conversion of ESBS

CMPEG/epoxy group (molar ratio)	DMA/epoxy group (wt %)	Epoxy conversion (%)
1.0	0	8.13
1.0	3	13.2
1.0	5	18.5
1.0	7	19.7
1.0	5	18.4
1.3	5	26.8
1.5	5	28.6

ESBS concentration = 10 g/100 mL; temperature = 70°C; time = 8 h.

1-g sample was accurately weighed into an iodometric titration flask. An HCl-acetone (1/80 v/v) solution (25 mL) was added. The flask was stoppered, and the mixture was stirred until the sample was dissolved. After it stood in the dark for 1 h, three drops of the indicator phenolphthalein were added, and the solution was titrated with a standard alcoholic KOH solution to a pink color:

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

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

The conversion of the epoxy group to the PEO graft was obtained according to the following equation:

$$\text{Epoxy conversion (\%)} = 100(E_0 - E_1)/E_0$$

where E_0 and E_1 are the original epoxy value and the epoxy value after the ring-opening reaction, respectively.

Characterization of the graft copolymer

The FTIR spectrum of SBS-g-PEO was taken with a Bruker Equinox 55 FTIR spectrophotometer (Ettlingen, Germany) with a KBr disc. The disc was coated with a solution of the sample, and this was followed by the evaporation of the solvent.

Properties of the graft copolymer

The water or oil absorbency of the graft copolymers was determined by the immersion of an accurately weighed sample (W_b) into water or kerosene at room temperature for 48 h and then the removal of the liquid with filter paper and the weighing of the sample (W_a):

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

The emulsifying property of the graft copolymers was represented by the emulsifying volume,⁶ which was determined as follows. A 0.2-g sample of a graft copolymer was dissolved in 30 mL of toluene and then added to 70 mL of water. The mixture was shaken thoroughly in a separating funnel for 5 min and then poured into a measuring cylinder covered with a watch glass. Overnight, the system separated into different layers. The emulsifying volume was taken as the total volume of the emulsion layer.

The phase-transfer catalysis property in a Williamson reaction was tested as follows.⁶ Toluene (40 mL), *n*-butyl bromide (2 mL), and 0.5 g of copolymer granules were added to a bottle containing potassium phenolate (PhOK; accurately weighed to 1.0 g). After being purged with N_2 , the system was heated at 90°C for 4 h with magnetic stirring. After the reaction, 50 mL of distilled water was added with stirring. The unreacted PhOK was titrated with standard HCl, with methyl red as an indicator, to determine the conversion of PhOK into butyl phenolate:

$$\text{Conversion of PhOK (\%)} = 100(W_{\text{PhOK}} - N_{\text{HCl}} \times V_{\text{HCl}} \times M_{\text{PhOK}/1000})/W_{\text{PhOK}}$$

where W_{PhOK} and M_{PhOK} are the weight (g) and molecular weight of PhOK, respectively, N_{HCl} and V_{HCl} are normality and the volume of HCl, respectively.

Blending of SBS with CHR in the presence of the graft copolymer as a compatibilizer

Blending SBS with CHR in a 50/50 weight proportion with or without a small amount of the graft copolymer was carried out on a hot mill at 170°C for 10 min, and compression molding was performed at 165°C under 15–20 MPa.

The tensile strength and ultimate elongation were measured on an RGD-0.5 tensile tester with a

TABLE II
Effects of the Reaction Temperature and Time on the Epoxy Conversion of ESBS

Temperature (°C)	Time (h)	Epoxy conversion (%)
70	6	10.8
70	7	14.9
70	8	18.5
70	10	20.4
65	8	12.3
70	8	14.9
75	8	18.5
80	8	20.4

ESBS concentration = 10 g/100 mL; DMA/ESBS = 5 wt %; CMPEG/epoxy (molar ratio) = 1 : 1.

TABLE III
Effect of the Concentration of ESBS on the Epoxy Conversion of ESBS

ESBS concentration (g/100 mL)	Epoxy conversion (%)
10	26.8
12	41.9
14	46.5

DMA/ESBS = 5 wt %; temperature = 70°C; time = 8 h; CMPEG/epoxy (molar ratio) = 1.3:1.

stretching rate of 250 mm/min. The permanent set was measured as the elongation percentage 3 min after the specimen was broken and reunited.

Scanning electron micrographs of the broken sections of the blends were taken with a JSM-5510LV electron microscope (Jeol, Tokyo, Japan) after the broken sections of the blend samples were vacuum-deposited with gold vapor.

RESULTS AND DISCUSSION

Effects of the synthesis conditions on the epoxy conversion of ESBS to the PEO graft

DMA can be used as a catalyst for the ring-opening reaction of epoxy groups with carboxylic acid, so it was tested as a catalyst for the ring-opening reaction of epoxy groups of ESBS with CMPEG to form a copolymer of SBS with PEO grafts. Table I shows that the addition of DMA can increase the epoxy conver-

sion. The epoxy conversion increases with an increasing amount of DMA quickly at first and then slowly beyond 5 wt %.

The effect of the CMPEG/epoxy group molar ratio on the conversion of epoxy groups of ESBS is also shown in Table I. The epoxy conversion increases with an increasing CMPEG/epoxy group molar ratio rapidly from 1.0 to 1.3 and then slowly from 1.3 to 1.5. The optimum molar ratio, higher than 1/1, is due to the heterogeneous reaction.

Table II shows that the epoxy group conversion increases with the reaction time obviously before 8 h and then increases slowly. To obtain a higher conversion of epoxy groups, a longer reaction time seems necessary.

Table II also shows the effect of the reaction temperature on the conversion of epoxy groups to PEO grafts. The epoxy conversion increases with an increase in the reaction temperature rapidly until 75°C and then gradually. Too high a reaction temperature may induce side reactions.

Table III indicates that the concentration of ESBS can enhance the epoxy conversion obviously. The epoxy conversion can rise from 26.8 to 46.5% when the ESBS concentration increases from 10 to 14 g/100 mL. A further increase in the concentration causes the reaction system to stir with difficulty.

The optimum conditions are a CMPEG/epoxy group molar ratio of 1.5, a DMA/ESBS concentration of 5 wt %, and an ESBS concentration of 12–14 g/100 mL at 75–80°C for 10 h.

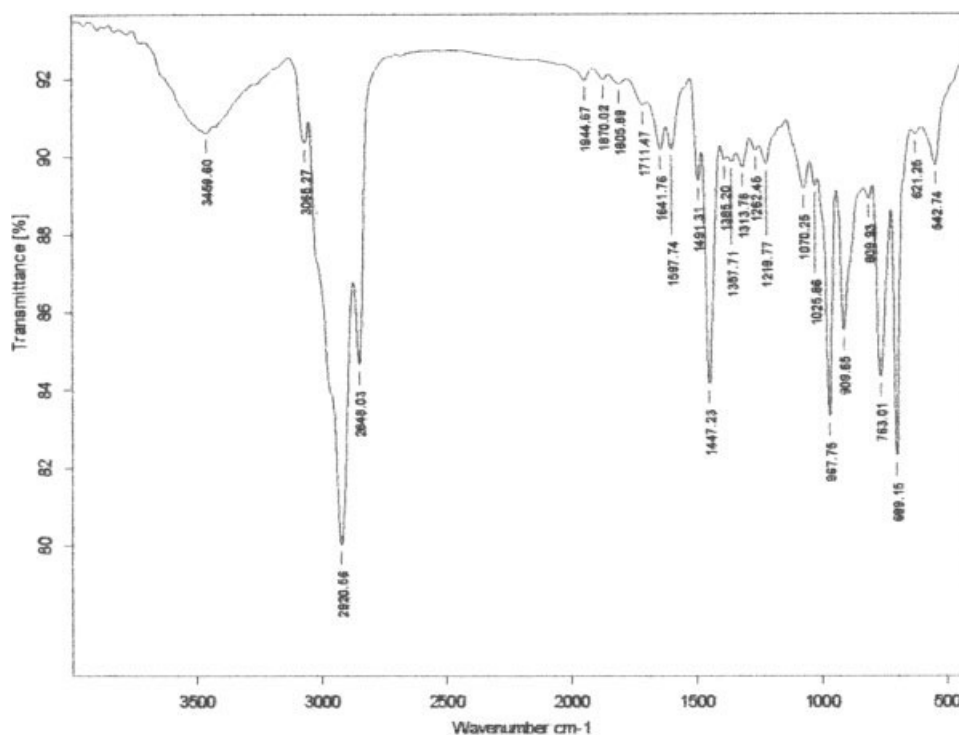


Figure 1 FTIR spectrum of SBS-g-PEO.

Characterization of SBS-g-PEO

The FTIR spectrum (Fig. 1) shows the absorption peak of an ether group of poly(ethylene glycol) at 1070 cm^{-1} and those of unreacted epoxy groups at 809 and 909 cm^{-1} . There also exist absorption peaks at 910 , 968 , and 730 cm^{-1} for the double bonds of polybutadiene segments and at 699 and 1450 cm^{-1} for the phenyl groups. The broad absorption peak at 3450 cm^{-1} exists for the OH group, which was formed simultaneously during the ring-opening reaction of epoxy groups.

Some properties of SBS-g-PEO

Table IV indicates that the water absorbency of the graft copolymer increases gradually with increasing PEO grafts because of the increase in hydrophilic segments. It also shows that with increasing PEO content, the graft copolymer in kerosene changes from a partially soluble state to the absorbance of kerosene. The oil absorbency of the graft copolymer decreases with increasing PEO content. This fact is attributed to the aliphatic oil resistance of PEO.

Because the graft copolymer contains both hydrophilic PEO grafts and a hydrophobic SBS backbone, it exhibits amphiphilic properties and can emulsify a toluene and water system. Table V shows that the emulsifying volume increases with an increase in the PEO content or weight of the graft copolymer because of the increase in the emulsifying centers. The emulsifying volume even reaches about 85 mL (the maximum emulsifying volume is 100 mL) when the PEO content reaches 0.20 – 0.27 mmol/g .

Because the graft copolymer contains both hydrophobic SBS backbones and hydrophilic segments of PEO, which can complex with alkali metal ions, it has been tested as a phase-transfer catalyst in the Williamson reaction between solid PhOK and liquid *n*-butyl bromide:

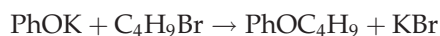


Table VI shows that only a small amount of PhOK reacts with *n*-butyl bromide in the absence of the graft copolymer. However, the conversion of PhOK increases obviously with increasing PEO content of

TABLE V
Emulsifying Property of SBS-g-PEO

Copolymer (g)	PEO (mmol/g)	Emulsifying volume (mL)
0.10	0.16	34.5
0.10	0.20	43.8
0.10	0.27	46.4
0.20	0.16	76.4
0.20	0.20	84.6
0.20	0.27	85.8

the graft copolymer. This indicates that the latter can complex the potassium ions of the phenolate and transfer them from the solid to the organic solution, thus enhancing the reaction between PhOK and *n*-butyl bromide. The higher the PEO content is or the longer the reaction time is, the higher the conversion of PhOK is. The latter reaches over 90% when the PEO content of the graft copolymer is 0.27 mmol/g and the reaction is carried out at 90°C for 5 h .

Blending of SBS and CHR with the graft copolymer as a compatibilizer

The graft copolymer can be used as a compatibilizer for the blending of SBS with CHR, which is a polar, oil-resistant, nonthermoplastic, vulcanizable elastomer. When a small amount of the graft copolymer is added to a blend of SBS and CHR in a weight proportion of $50/50$, the mechanical properties of the blend are improved. The tensile strength and ultimate elongation of the blend increase with an increasing amount of the graft copolymer added, as shown in Table VII. Especially when the added amount of the graft copolymer reaches $3\text{ wt}\%$ of the blend, both the tensile strength and the ultimate strength of the blend increase about 1.7 times. However, the permanent set is kept at about 20% . Thus, the blends behave as thermoplastic elastomers. The improvement of the mechanical properties of the blends by a small amount of the graft copolymer can be attributed to the interfacial adhesion via the graft copolymer because on the one hand the SBS backbones of the graft copolymer are miscible with the SBS phase and on the other hand there exists an interaction between the ether linkage of CHR and the PEO grafts of the graft copolymer. However, if

TABLE IV
Effect of the PEO Content of SBS-g-PEO on the Water Absorbency and Kerosene Absorbency of SBS-g-PEO

PEO (mmol/g)	Water absorbency (%)	Kerosene absorbency (%)
0.16	28.5	Swelled a lot and difficult to measure
0.20	42.1	289
0.27	60.7	187

TABLE VI
Effect of the PEO Content on the Phase-Transfer Catalyst Efficiency of SBS-g-PEO

PEO (mmol/g)	PhOK conversion at 3 h (%)	PhOK conversion at 5 h (%)
0	5.64	8.96
0.16	28.7	63.4
0.20	34.1	75.0
0.27	41.6	91.5

the graft copolymer is used at a concentration of more than 4 wt % with respect to the blend, the tensile strength of the blend decreases. This is probably because the PEO grafts of the graft copolymer at the surface of the SBS phase are shielded by the PEO grafts of the excess copolymer used. A blend containing 3 wt % graft copolymer absorbs only 58.5% kerosene in 48 h at room temperature.

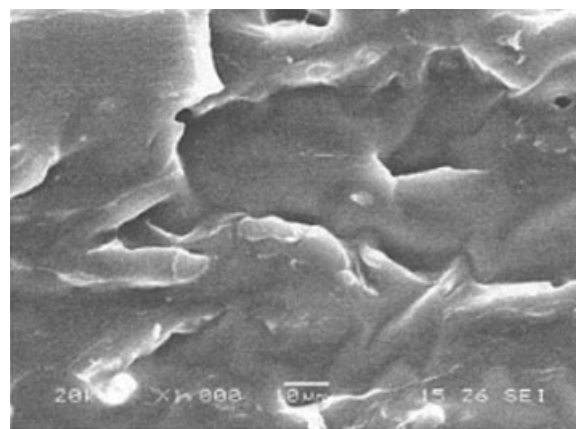
The enhanced compatibility of the two components by the graft copolymer can be demonstrated by scanning electron microscopy (SEM). SEM micrographs of the surface of broken sections of blends of SBS and CHR without or with the addition of the graft copolymer as a compatibilizer are shown in Figure 2(a,b). The surface of the broken section of the blend containing the graft copolymer seems smoother than that without the graft copolymer. Thus, it implies that the graft copolymer improves the interfacial adhesion between the surfaces of the two phases.

CONCLUSIONS

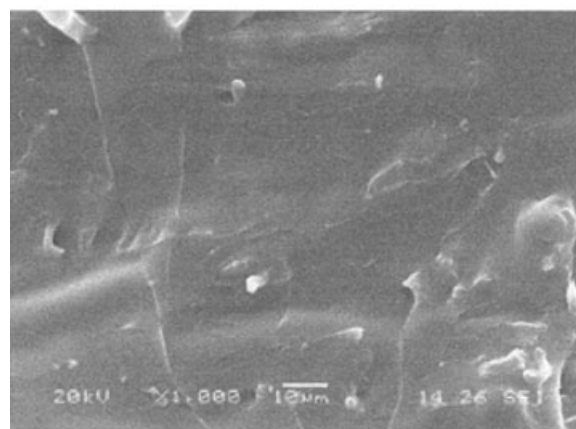
A novel method for the preparation of a graft copolymer of SBS with PEO grafts has been developed through a ring-opening reaction of ESBS with CMPEG. During the ring-opening reaction, DMA as a ring-opening catalyst is needed to enhance the conversion of epoxy groups to PEO grafts. The optimum conditions are a CMPEG/epoxy group molar ratio of 1.5, a DMA/ESBS concentration of 5 wt %, and an ESBS concentration of 12–14 g/100 mL at 75–80°C for 10 h. The FTIR spectrum demonstrates the characteristic groups of SBS-g-PEO. With increasing PEO content, the water absorbency of the graft copolymer increases, whereas its oil absorbency decreases. The graft copolymer exhibits a good emulsifying property and good phase-transfer catalysis behavior. The graft copolymer behaves as a good compatibilizer for blending equal amounts of SBS and oil-resistant CHR. In the presence of a 3% concentration of the graft copolymer, the blend exhibits much better mechanical properties and solvent resistance than the blend without the graft copolymer. SEM

TABLE VII
Effect of the Amount of SBS-g-PEO on the Mechanical Properties of SBS and CHR Blends

SBS-g-PEO/ blend (%)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	8.64	856	16
1	10.4	964	17
2	12.4	1350	20
3	14.1	1490	23
4	13.3	1540	27
5	12.2	1460	24



(a)



(b)

Figure 2 SEM micrographs of broken sections of SBS/CHR blends (a) without or (b) with SBS-g-PEO at a magnification of 1000 \times .

micrographs indicate improved compatibility between the two components in the presence of the graft copolymer.

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