

Synthesis of Amphiphilic Graft Copolymers of SBS with Acrylamide and Study of Their Properties

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Received 9 April 2004; accepted 5 September 2004

DOI 10.1002/app.21444

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Graft copolymerization of SBS in the form of sodium ionomer with acrylamide in emulsion using benzoyl peroxide as initiator and sodium ionomer of maleated SBS as a self-emulsifier, which can form a stable cyclohexane/water emulsion with AM without using any other emulsifier, was carried out. Factors affecting the graft copolymerization were studied. The grafting % can reach about 15%. Emulsifying properties of sodium ionomer of maleated SBS and the graft copolymer, as well as the compatibilizing effect of the graft copolymer in blending polyvinyl chloride (PVC) with SBS, were studied. The sodium ionomer of maleated SBS, the graft copolymers, and the blends were characterized with IR and DSC. The results showed that water absorbency and emulsifying volume increase obviously after graft copolymerization with AM. 0.2 g of the graft copolymer containing 14 wt % PAM grafts can emulsify a mixture of 30 mL toluene

and 70 mL water completely. The graft copolymer can be used as an effective compatibilizer in the blending of PVC and SBS, more effective than the sodium ionomer of maleated SBS. Only 2 wt % of the copolymer based on the blend used in blending is enough to raise the tensile strength three times. The blends with weigh ratios of PVC/SBS at 3/7–4/6 in the presence of the graft copolymer behave as thermoplastic elastomers with a tensile strength of 14 MPa, an ultimate elongation of 750%, and a permanent set of 17%. Glass transition temperatures of the blend shifted inward in the presence of the graft copolymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1248–1253, 2005

Key Words: graft copolymers; emulsion polymerization; SBS; acrylamide; emulsifying property; compatibilization

INTRODUCTION

SBS is a (styrene–butadiene–styrene) triblock copolymer and extensively used as a thermoplastic elastomer and a melt adhesive. It is a nonpolar polymer and is not compatible with a polar substance. Hence polar modification of SBS has been given much attention. However, until now, most research has been concentrated on the maleation of SBS with maleic anhydride in organic solution or in the melt^{1–3} or graft copolymerization of SBS with (meth)acrylic acid in organic solution. Wilhelm and Felisberti⁴ studied the bulk modification of SBS with maleic anhydride (MAH) in a mixing chamber of a Haake rheomixer. High grafting efficiency was achieved when the ratio of peroxide and MAH concentration was high, but the gel content also increased. Wilkie et al.⁵ reported that methacrylic acid can be grafted onto SBS either by a photochemical process or by chemical initiation. The amount of grafting is similar in both procedures. Almost no graft copolymerization of SBS with acrylamide (AM) in solution or emulsion was reported, because acrylamide

neither can be dissolved in the organic solvent for SBS nor can be graft copolymerized on SBS in stable emulsion. Geuskens and Kanda⁶ reported the grafting of (meth)acrylic acid and acrylamide on the surface of SBS films using polymeric hydroperoxide of SBS as initiator, which was photosensitized by anthracene. Geuskens et al.⁷ showed that reaction of SBS with photogenerated singlet oxygen produces clusters of polymeric hydroperoxides. At 100°C they decompose about 100 times faster than low molecular weight hydroperoxides. SBS hydroperoxides were used to initiate the grafting of acrylamide in boiling aqueous solutions of that monomer. Grafting is restricted to the surface of the material, since acrylamide does not diffuse into SBS. After grafting, its surface becomes very hydrophilic. Lee and Chen⁸ studied the grafting polymerization of *N*-isopropylacrylamide onto SBS using benzoyl peroxide as initiator to improve the water absorbency and thermosensitivity of SBS. Antony and De⁹ indicated that the introduction of ionic groups into the hydrogenated SBS improves the thermal stability and high temperature performance. Ghosh et al.¹⁰ sulfonated the maleated SEBS block copolymer (with 1% MAH content) and neutralized by different metal acetates to form ionomers containing both carboxylate and sulfonate anions on the same polymer backbone.¹⁰

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This article deals with the graft copolymerization of SBS in the form of sodium ionomer of maleated SBS with acrylamide in an emulsion using sodium ionomer of maleated SBS as a self-emulsifier, which can form a stable hexane/water emulsion with AM, using benzoyl peroxide as initiator. The sodium ionomer of maleated SBS and the graft copolymers were characterized. Emulsifying properties of sodium ionomer of maleated SBS and the graft copolymer, as well as the compatibilizing effect of the graft copolymer in blending polyvinyl chloride with SBS, were studied.

EXPERIMENTAL PROCEDURES

Materials

All the reagents and solvent were chemically pure. Linear type SBS with molecular weight of about 1×10^5 and styrene/butadiene = 3/7 wt/wt was supplied by Yue-Yang Synthetic Rubber Factory in China. Polyvinyl chloride PVC-1300 was purchased from Gedian Chemical Technological Co.

Maleation of SBS and preparation of sodium ionomer of maleated SBS

100 g SBS and 10 g MAH were dissolved in 800 mL toluene. Under a nitrogen atmosphere, a 200 mL toluene solution of 1.5 g benzoyl peroxide was then dropped into the solution within 0.5 h during stirring. The maleation was carried out at 75°C for 4 h. A small amount of the maleated product was taken out, precipitated, and washed three times with 0.1% antioxidant 264-containing acetone for the purpose of determining the MAH content. An aqueous 16 wt % NaOH solution equivalent to the MAH used in maleation during stirring was added to most of the maleated solution. The neutralization reaction was continued for 0.5 h with stirring. The neutralized product was precipitated with acetone, containing 0.1% antioxidant 264. The precipitated rubbery product was washed with water three times to remove excess NaOH and sodium maleate. The sodium ionomer of maleated SBS then was dried under an infrared lamp and in a vacuum dryer at 60°C.

For determination of MAH content, the purified and dried sample of maleated SBS was accurately weighed (W). The MAH content was determined by adding excess 0.1M alcoholic KOH solution and back titrated with 0.1M alcoholic HCl solution, using phenolphthalein as indicator. The MAH content of the maleated SBS sample can be calculated as follows:

$$\text{MAH content, \%} = (N_{\text{KOH}} \times mL_{\text{KOH}} - N_{\text{HCl}} \times mL_{\text{HCl}}) \times 49.03 / (10 \times W)$$

Graft copolymerization of sodium ionomer of maleated SBS (SBSI) with acrylamide

The SBSI containing 6.7 wt % MAH was dissolved in cyclohexane with stirring to about 9% (w/v) concentration. To the solution was added an aqueous solution of acrylamide with vigorous stirring to form an emulsion. The emulsion was purged with nitrogen gas and heated to 75°C. A benzoyl peroxide solution was then added and the polymerization was carried out for 6 h. The polymerization was terminated by adding a small amount of *p*-hydroxyphenol. The reaction mixture was precipitated with ethanol. The precipitate was filtered, washed with acetone three times, dried, and weighed. The dried crude product was purified by extraction with water three times, filtered, dried, and weighed. Conversion of AM and grafting % (or PAM content) were calculated as follows:

$$\text{Conv. of AM (\%)} = (\text{wt of crude product} - \text{wt of ionomer}) \times 100 / \text{Charged wt of AM} \quad (1)$$

$$\text{Grafting \%} = (\text{wt of purified product} - \text{wt of ionomer}) \times 100 / \text{wt of purified product} \quad (2)$$

Characterization of the ionomer and graft copolymer

IR spectra of the sodium ionomer of maleated SBS and its graft copolymer with AM was taken with a Equinox 55 FTIR spectrophotometer, using a KBr disc, coated with a solution of the sample, followed by drying. The glass transition temperature was determined with differential scanning calorimeter made by Mettler Toledo Co. with a heating rate of 20°C/min and a sample weight of about 10 mg under nitrogen.

Emulsifying properties

Emulsifying properties of the polymers are represented by emulsifying volume,¹¹ which was determined as follows: 1.0 g sample of SBSI or 0.2 g sample of SBSI-g-PAM was dissolved in 30 mL toluene and then added to 70 mL water. The mixture was shaken thoroughly for 5 min and poured into a measuring cylinder covered with a watch glass. Overnight, the system separated into two layers. The emulsifying volume is taken as the total volume of toluene plus water minus the volume of the lower water layer.

Water absorbency

About 1.0 g of film sample was accurately weighed (W_b) and immersed in distilled water at room temperature for 24 h and then taken out. After removing water from the surface, the sample was accurately

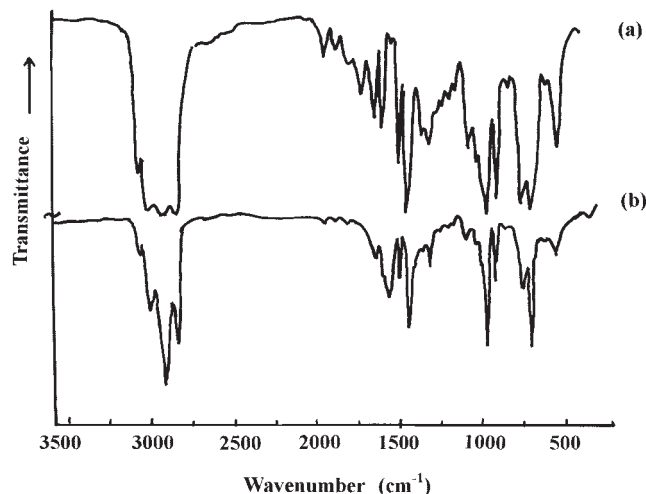


Figure 1 IR spectra of (a) maleated SBS and (b) sodium ionomer of the maleated SBS.

weighed (W_a). The water absorbency was calculated as follows:

$$\text{Water absorbency (\%)} = (W_a - W_b) \times 100 / W_b \quad (3)$$

Blending of polymers

SBS was first mixed with 1 wt % antioxidant 264 on a hot mill at 100°C and blended with different amounts of PVC containing 1 wt % lead stearate and different amounts of the graft copolymer at 150°C for 15 min. The blend then was molded on a hot press at 155–160°C under 20 MPa and cut into dumbbell-like specimens.

Measurement of mechanical properties

The tensile strength and ultimate elongation of the specimens were measured on a DL-2500 Tensile tester with an extension rate of 250 mm/min at 25 ± 5°C. The permanent set was measured as the % elongation 3 min after the specimen was broken and reunited.

RESULTS AND DISCUSSION

Characterization and some properties of the sodium ionomer of maleated SBS

Figures 1(a) and (b) illustrate the FTIR spectra of maleated SBS and SBSI, respectively. The former (a) shows the characteristic absorption peak at 1720 cm^{-1} for C=O group, whereas the latter (b) shows the characteristic absorption peak at 1405 and 1600 cm^{-1} for the carboxylate groups. Both spectra indicate the absorption peaks at 699, 910, 1490, and 3000 cm^{-1} for the phenyl ring and 3060 and 1025 cm^{-1} for double bonds.

TABLE I
Effect of MAH Content on Emulsifying Property and Water Absorbency of the Sodium Ionomer of Maleated SBS

MAH content (%)	Emulsifying volume (mL)	Water absorbency (%)
2.97	36.1	11.2
5.48	48.3	14.4
6.74	59.2	16.0
7.21	61.4	16.5
10.2	66.9	18.2
15.2	72.2	23.1

Table I shows the emulsifying property and water absorbency of 1 g maleated SBSI with different MAH contents. It can be seen that, with increasing MAH content, both water absorbency and emulsifying volume increase. The emulsifying volume can represent the emulsifying property of the polymer for the oil/water system. The higher the emulsifying volume, the better is the emulsifying property. This fact indicates that formation of COONa groups on SBS increases the polarity or hydrophilic property of SBS. When the ionomer of SBS was dissolved in cyclohexane to about 9% w/v and mixed with water with vigorous stirring, the mixture formed an emulsion with high stability, even at 75°C. This fact implies that no emulsifier is needed during graft copolymerization of SBSI with AM in emulsion.

Factors affecting the graft copolymerization of SBSI with AM in emulsion

Table II lists the effects of charging amounts of BPO and AM on the graft copolymerization of SBSI with AM. It can be noted that, with increasing the charging amount of initiator, BPO, both conversion of AM and grafting % increase. However, the increase of AM conversion is more rapid than that of grafting %. This fact denotes that excess initiator prefers to initiate homopolymerization of AM than to initiate the graft

TABLE II
Effects of Charging Amounts of Benzoyl Peroxide and Acrylamide on Graft Copolymerization at 75°C for 6 h

BPO/SBSI (wt %)	AM/SBSI (wt %)	AM conversion (%)	Grafting %
0.6	0.4	47.6	5.90
1.0	0.4	58.4	9.81
1.4	0.4	70.3	14.2
1.8	0.4	Gel	Gel
1.4	0.2	84.7	7.84
1.4	0.3	81.2	11.1
1.4	0.4	70.3	14.2
1.4	0.5	62.8	15.6
1.4	0.6	54.9	15.9

TABLE III
Effects of Copolymerization Time and Maleated Content of SBSI on the Graft Copolymerization^a

Time (h)	Maleic anhydride content of SBSI (wt %)	AM conversion (%)	Grafting %
2	6.74	42.6	5.48
4	6.74	58.4	11.2
6	6.74	70.3	14.2
8	6.74	87.1	14.7
6	2.93	68.6	13.6
6	6.74	70.3	14.2
6	15.2	64.7	12.6

^a BPO/SBSI = 1.4 wt %, AM/SBSI = 0.4/1, 75°C.

copolymerization of AM on SBS. At BPO/SBSI = 1.8 wt %, some gels occur in the polymerization system.

As also shown in Table II, when the charging amount of AM increases, the AM conversion decreases, whereas the grafting % increases rapidly at first and then slowly until it almost levels off. This fact implies that excess AM is not favorable to grafting copolymerization, but enhances only the homopolymerization.

Table III lists the effects of copolymerization time and the maleation degree of SBSI on the AM conversion and grafting %. With increasing copolymerization time, AM conversion increases rapidly at first and then gradually. But the grafting % increases obviously at first, but almost levels off after 6 h. This implies that, after 6 h, most AM converts into homopolymer.

With increasing MAH content of the SBSI, there occurs a maximum value both in grafting % and AM conversion. This phenomenon is probably due to two factors. The first factor is that, the higher the MAH content of the SBSI, the better are the emulsifying properties of the SBSI, thus decreasing the size of emulsion particles and favoring the grafting copolymerization. The second factor is that, the higher the MAH content, the lower are the double bonds remaining in SBS. Hence, if the MAH content is too high, fewer double bonds, that can be copolymerized with AM remain in SBS.

Characterization of the graft copolymer of SBSI with AM

The purified graft copolymer was characterized by FTIR spectrum, as shown in Figure 2. The absorption peaks at 1640 cm⁻¹ exist for COO⁻ groups, those at 699, 910, 1490, and 3000 cm⁻¹ for the phenyl ring and those at 3060 and 1025 cm⁻¹ for double bonds. Absorption peaks at 1560/3390 and 1440 cm⁻¹ belong to the NH₂ and C—N groups, respectively. This spectrum shows that the purified product really contains both ionomers of maleated SBS units and of the polyacrylamide units.

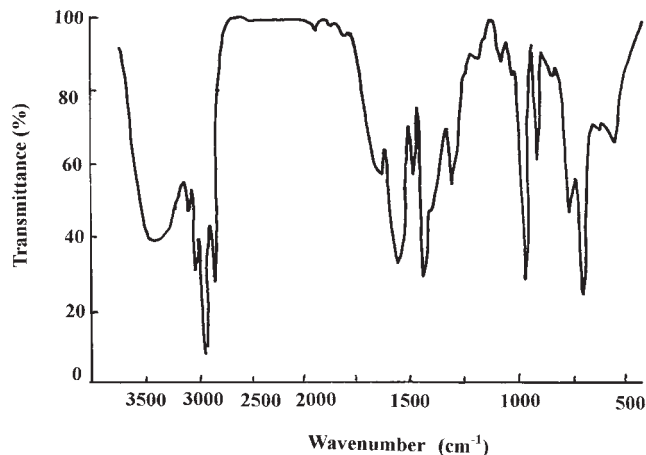


Figure 2 IR spectrum of the graft copolymer of SBS with polyacrylamide.

DSC curves of the purified product indicated three glass transition temperatures at -84.8, 50.8, and 90.5°C, which correspond to T_g s of polybutadiene, polyacrylamide, and polystyrene, respectively. This phenomenon implies that the graft copolymer is a multiphase copolymer.

Water absorbency and emulsifying properties of SBSI-g-PAM

Both the water absorbency and the emulsifying properties of SBSI increase obviously after graft copolymerization with AM, as shown in Table IV. This phenomenon can be interpreted as the fact that PAM is much more hydrophilic than the sodium carboxylate group. The emulsifying volume increases with the grafting % of AM obviously at first and then gradually. At a grafting % of 14.2% PAM, the grafting copolymer can emulsify the mixture of toluene and water completely.

Compatibilizing effect of SBSI-g-PAM on the blends of PVC and SBS

SBS is a nonpolar polymer, whereas PVC is a polar polymer. The compatibility of the two polymers is

TABLE IV
Emulsifying Property and Water Absorbency of the Graft Copolymer of SBSI^a versus Grafting Ratio of PAM

Grafting ratio (%)	Emulsifying volume ^b (mL)	Water absorbency (%)
0	48.3	14.4
5.35	90.9	33.1
7.32	94.1	77.3
12.6	98.2	82.8
14.2	100	95.2

^a SBSI with MAH content of 5.48 wt %.

^b 0.2 g sample was tested for the graft copolymer, but 1.0 g sample was tested for the first sample of SBSI without PAM grafts.

TABLE V
Mechanical Properties of SBS/PVC Blends in the Presence of 2 wt % Lead Stearate and 0.5% Antioxidant 264 With or Without the Graft Copolymer or SBSI as Compatibilizer

Graft copolymer/ blend (wt ratio)	SBS/PVC (wt ratio)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	60/40	5.26	610	17
1	60/40	9.32	715	20
2	60/40	14.1	740	19
3	60/40	11.0	725	24
4	60/40	7.83	670	20
5	60/40	5.97	555	13
2	100/0	9.90	1060	36
2	85/15	10.6	880	29
2	70/30	14.5	750	17
2	60/40	14.1	740	17
2	40/60	18.6	170	3
2	30/70	24.3	25	2
2	15/85	31.8	14	1
2 ^a	60/40	7.14	655	14

^a SBSI containing 6.74 wt % MAH used as compatibilizer instead of the graft copolymer.

poor. SBSI-g-PAM may be used as a compatibilizer for the two polymers, because the PAM side chains can be compatible with PVC through hydrogen bonds.

Table V shows that, when the weight ratio of SBS/PVC is 60/40, the tensile strength and the ultimate elongation of the blend are only 5.26 MPa and 610%, respectively. However, if a small amount of the graft copolymer is added to the blend during melt blending, the mechanical properties of the blends are improved significantly. This is attributed to the fact that the graft copolymer plays the role of the compatibilizer, the PAM grafts of which can form hydrogen bonds with the PVC phase, whereas most of the backbones of maleated SBS are miscible with the SBS phase, thus connecting the two phases at the interfaces. With increasing the amount of graft copolymer, both the tensile strength and the ultimate elongation of the blend increase. The optimum amount of the graft copolymer is 2 wt % based on the blend. According to the mechanical properties, the blends behave as thermoplastic elastomers. But if the graft copolymer was used at more than 3 wt % of the blend, both the tensile strength and the ultimate elongation diminish. Table V also shows that, as the weight ratio of SBS/PVC decreased in the presence of 2 wt % graft copolymer, the tensile strength of the blend increased and the ultimate elongation decreased, i.e., the blend changed from a thermoplastic elastomer to toughened plastics, which is due to the change of continuous phase from SBS to PVC. If the ionomer without grafting with AM was used as the compatibilizer, the tensile strength of the blend is only half of that using the graft copolymer as the compatibilizer as shown in Table V.

Comparison of DSC curves between the blends with and without the graft copolymer used as compatibilizer

Comparison of DSC curves of the blends with or without the graft copolymer or SBSI as compatibilizer indicated that the two glass temperatures of the blend shifted inward from $-85.5, 89.8$ to $-85.8, 82.5^\circ\text{C}$ in the presence of 2 wt % of graft copolymer. The inward shift of T_g denotes that the graft copolymer enhances the compatibility of SBS and PVC due to the improvement of interfacial adhesion. However, the two glass temperatures of the blend shifted less inward from $-85.5, 89.8$ to $-85.3, 84.4^\circ\text{C}$ in the presence of 2 wt % of SBSI.

CONCLUSION

In the graft copolymerization of SBS in the form of sodium ionomer with acrylamide in emulsion, using benzoyl peroxide as an initiator and SBSI as a self-emulsifier, the optimum charging amounts of BPO and AM used are 1.4 and 20–30 wt % based on SBSI, respectively. The optimum MAH content of SBSI and copolymerization time are 6.7 wt % and 6 h, respectively. The grafting % can reach about 15%. Water absorbency and emulsifying volume of the SBSI increase obviously after graft copolymerization with AM. 0.2 g of the graft copolymer containing 14 wt % PAM grafts can emulsify a mixture of 30 mL toluene and 70 mL water completely. The graft copolymer can be used as an effective compatibilizer in the blending of PVC and SBS, more effectively than SBSI. Only 2 wt % of the graft copolymer based on the blend is enough to raise the tensile strength of PVC/SBS blend three times. The blends with weight ratios of PVC/SBS at

30/70–40/60 also behave as thermoplastic elastomers with a tensile strength of 14 MPa, an ultimate elongation of 750%, and a permanent set of 17 %, whereas those with weight ratios at 60/40–85/15 behave as toughened plastics. Glass transition temperatures of the blend shifted inward in the presence of the graft copolymer, which indicates that the two components of the blend become more compatible.

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