Epoxidation of Styrene/Butadiene Star Block Copolymer by Different Methods and Characterization of the Blends with Epoxy Resin

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Summary: A star shaped polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) block copolymer was subjected to epoxidation reaction using different reagents such as *m*-chloroperoxy benzoic acid (MCPBA), peracetic acid (PAA), performic acid (PFA) and hexaflouro-isopropanol (HFIP). All the methods led to the targeted modification of the block copolymer satisfactorily, some of them also accompanying rapid side reactions. The epoxidized polymer was then blended with epoxy resin comprising diglycidyl ether of bisphenol-A in presence of methylene dianiline (MDA) as hardener. The mixing of the epoxidized block copolymer into the epoxy resin led to the formation of well dispersed uniform blend morphology and imparted enhanced thermostability and ductility to the blends. A brittle-to-ductile transition was observed in the blends.

Keywords: block copolymer; electron microscopy; FTIR spectroscopy; microphase separation; polymer blend

Introduction

During the last several decades, block copolymers have been developed as innovative materials with specific mechanical, optical and electronic properties. Those properties evolve mainly due to the presence of inherent nanostructured morphologies which are adjustable by volume fraction of different components of the copolymer, interaction between different monomers and block copolymer chain architecture.[1–5] On using them as a blend component in combination with other polymers and optimizing the processing parameters, these block copolymers can template nanostructured morphology in the blends as proved by several recent studies.[6–13] Due to presence of the nanostructures, the blends of block copolymer with epoxy resins exhibit enhanced toughness. Various epoxy resin systems of diglycidyl ether of bisphenol-A (DGEBA) with diblock,[9] triblock,[10] star block[11,12] and tetrablock[13] copolymers in presence of aromatic amine as a hardener were investigated in the past. Nevertheless, the resulting blends represent a complex system with many parameters to be adjusted for the successful establishment of their structure properties correlations. In such studies, it has been demonstrated that the butadiene blocks of the polystyrene/polybutadiene block copolymers can be functionalized by various epoxidation methods. Then, the chemically modified block becomes miscible with the epoxy resin whereas

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styrene block remains immiscible. One of the main challenges of such studies has been to establish standard pathways to generate typical morphologies in the blends. In such processes, the optimization of microstructures of the chemically modified chains is an important task. In this work, we report the epoxidation of a styrene/butadiene block copolymer using different methods. The epoxidized samples were then blended with epoxy resins and characterized by FTIR spectroscopy, thermogravimetric analysis and electron microcopy.

Experimental Part

Materials

The polymer used in this work was star shaped polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) block copolymer with molecular weight (M_w) of 120,000 g/mol and polybutadiene (PB) weight fraction of 70% (courtesy of Dr. Robert Bening, Kraton Polymers, Houston, TX, USA). Analytical grade toluene (99%), formic acid (85%), polyethylene glycol (PEG-400), hydrogen peroxide (30%), methanol (99.5%), dicholoromethane (99%), chloroform (99%), *m*- choloperoxy benzoic acid (MCPBA), peracetic acid (39%), hexafluoro-isopropanol (HFIP), phenyl arsonic acid, sodium bicarbonate, sodium sulphate, diglycidyl ether of bisphenol-A (DGEBA) and methylene dianiline (MDA) were purchased from Sigma-Aldrich, Germany and were used without further purification.

Epoxidation of the SBS Star Block Copolymer

The block copolymer was epoxidized using four different methods. The modified sample has been named as eSBS. In each case, the degree of epoxidation was 50% by weight of total polybutadiene.

I. Performic Acid (PFA) Method

The SBS block copolymer was epoxidized by following the standard procedures discussed in literature.[14,15] Five grams of the SBS sample were dissolved in 50 ml of toluene in 250 ml three necked round bottom flask equipped with a magnetic stirrer, thermometer and reflux condenser. Stoichiometric amount of formic acid, hydrogen peroxide and two drops of PEG-400 were added to the polymer solution and the performic acid was formed *in situ*. The solution was heated slowly to 60 °C under constant stirring for 4 hours. The solution was cooled to room temperature and the resulting polymer was coagulated by adding methanol. The residue was filtered and dried.

II. m-Chloroperoxy Benzoic Acid (MCPBA) Method

The SBS block copolymer was epoxidized by following the standard procedure.[16] One gram of the SBS was dissolved in 25 ml of dichloromethane in three necked flask and equivalent amount of MCPBA was added slowly in the solution at 0 °C. The mixture was stirred vigorously for one and half hours under inert atmosphere. The completion of reaction was tested by potassium iodide-starch paper. After the completion of the reaction, the mixture was filtered. The filtrate was extracted with saturated aqueous sodium bicarbonate solution and was then dried with sodium sulphate and filtered. The organic portion of the solution was separated and the epoxidized SBS was recovered by removing solvent in a rotary evaporator and residue was dried.

III. Peracetic Acid (PAA) Method

The SBS block copolymer was epoxidized by following the procedures discussed elsewhere.[17] One gram of SBS was dissolved in 25 ml of dichloromethane and taken in three necked flask with magnetic stirrer. The molar ratio of SBS and peracetic acid was 1:1 and the calculated amount of the peracetic acid was added in the solution at 0 °C under inert atmosphere. The mixture was allowed to react for one and half hours. The completion of the reaction was tested by the potassium iodide/starch paper. The rest of the procedure was same as for the MCPBA method.

The conversion of the SBS into eSBS (i.e., the copolymer comprising epoxide groups) has been schematically depicted in Scheme 1.

IV. Hexafluoro-Isopropanol (HFIP) Method

The SBS block copolymer was subjected to epoxidation reaction using literature method.[18] 2 grams of SBS were dissolved in 25 ml of chloroform in three necked flask. The solution was stirred with a magnetic stirrer at 0 °C for 30 min. Then, 22 ml of hexafluoro isopropanol was added slowly into the solution followed by addition of 0.04 g of phenylarsonic acid as catalyst into the reaction mixture. After 10 min, white precipitate was observed. The mixture was heated up to 60 °C for 2 hours. The rest of the procedure was the same as in MCPBA method.

Fabrication of Blends

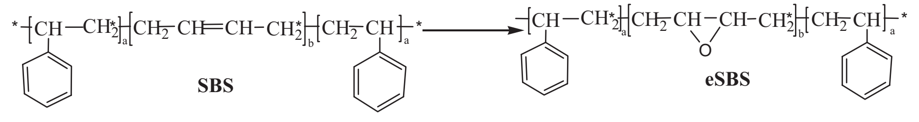
Using the epoxidized SBS block copolymer (eSBS), the blends with different compositions were prepared with diglycidyl ether of bisphenol-A (DGEBA) epoxy resin. The pure epoxy resin was prepared by mixing equivalent amounts of DGEBA and amine hardener (2 mol of epoxy resin and 1 mol of methylene dianiline, MDA; epoxy resin to MDA ratio of 2:1) under constant stirring. The blends with eSBS were prepared with epoxy resin/eSBS composition ratio of 70/30. For the blends preparation, the components were dissolved separately in toluene. Then, both the solutions were mixed and the mixture was heated to 110 °C for complete evaporation of the solvent. Then the residue was mixed together with appropriate amount of MDA. As a result, chemically cross-linked network-structured thermosetting blends were formed. The content comprising the pure resin as well as the blends was poured into in cylindrical Teflon molds and pre-cured at 80 °C for 12 hours and post-cured at 140 °C for another 12 hours. The reactions involved are illustrated schematically in Scheme 2. It should be however noted that the reactions presented are only schematic as the reactions of different epoxy groups and amine groups have random character.

Characterization Methods

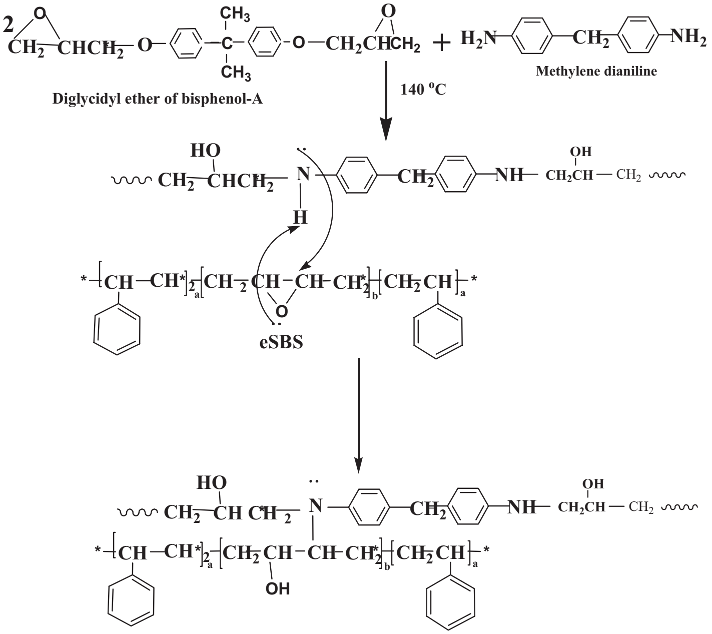
Fourier transform infrared (FTIR) spectrometer (Affinity 2000 Spectrometer, Shimadzu Corporation, Japan) in ATR mode was used for recording the IR spectra within a wavenumber range of 600–4000 cm^{-1}. *Scanning electron microscopy* (SEM; JSM 6300 manufactured by JEOL, Japan) was used to study the microscopic structures using the cryo-fractured surface of the samples. For the SEM studies, the specimens were broken under liquid nitrogen and fracture surfaces sputter-coated with a few nanometers thick gold film. *Thermogravimetric analysis* (TGA) of the samples was carried out at a heating rate of 10 °C/min under dry nitrogen atmosphere using TGA 209 balance (Netzsch, Germany) in the temperature range of 20–800 °C.

Results and Discussion

The FTIR spectra of block copolymers epoxidized in different ways are compared



Scheme 1.
Scheme of epoxidation reaction of SBS copolymer; the C=C double bonds were changed into the epoxide groups in the eSBS.



Scheme 2.

Reactions depicting the formation of MDA cured epoxy resin and the blend with eSBS.

with the spectrum of pure SBS polymer in Fig. 1. For the pure copolymer, the peaks centered at 965 cm^{-1} and 910 cm^{-1} can be clearly visible. Those peaks correspond to the C-H bending vibrations of vinyl side chain ($CH_2=CH$-) and *trans*-1,4-polybutadiene, respectively.[19] The peak at 1240 cm^{-1} represents the *in-plane* bending of aromatic C-H bonds. The peaks around 1450 cm^{-1} and 1490 cm^{-1} represent the C-H bending vibrations of CH_2 groups and the bands at 2850–3028 cm^{-1} correspond

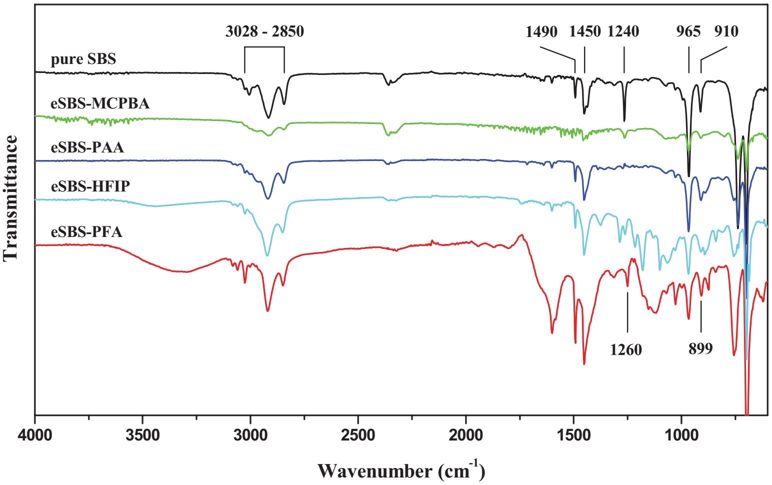


Figure 1.

FTIR spectra of eSBS samples prepared by different methods compared with pure SBS copolymer.

to C-H stretching vibrations of CH_2 and CH_3 groups.

The epoxidized copolymers (i.e., the eSBS samples) prepared by different methods show remarkable changes in the FTIR spectra (see Fig. 1). Let us carefully look at the peaks centered around 899 cm^{-1} and 1260 cm^{-1} which have been assigned to half and whole of the epoxy rings stretching, respectively.[14,19] The presence of those peaks in the epoxidized samples confirms, thus, the occurrence of desired modification.

In addition, the drastic decrease in intensities of the peaks centered around 965 cm^{-1} and 910 cm^{-1} in all the epoxidized samples can be observed, which correspond to the C-H bending vibrations of vinyl side chain ($CH_2 = CH$-) and *trans*-1,4-polybutadiene, respectively.[19] The peak at 1240 cm^{-1} represents the *in-plane* bending of aromatic C-H bonds, respectively.[19] Thus, the presence of those peaks confirms further the success of the epoxidation of the block copolymer by different methods. It should be noted that the statements of peak assignment to different functional groups are rather qualitative as the peaks were not normalized to compare quantitatively the relative effectiveness of different epoxidation methods.

In summary, we can conclude that all the methods introduced in the experimental section were found to be suitable for the epoxidation of the block copolymer, the HFIP method being the most time-effective and the PFA method the most cost-effective methods. However, it should be noted, that some strange peaks appear around 950–1400 cm^{-1} range in the eSBS samples prepared by PFA and HFIP methods indicating the occurrence of side reactions. Thus, those methods are not optimal for the epoxidation of styrene/butadiene block copolymers. We find the MCPBA method to be practically the most suitable one for the purpose in terms of time, cost and ease of controlling reaction conditions.

Thermogravimetric analysis (TGA) plots of some of the blends have been compared with the pure polymers in Fig. 2. The pure epoxy resin begins the mass loss at about 180 °C with a sharp mass loss at 411 °C. This shows that the epoxy resin

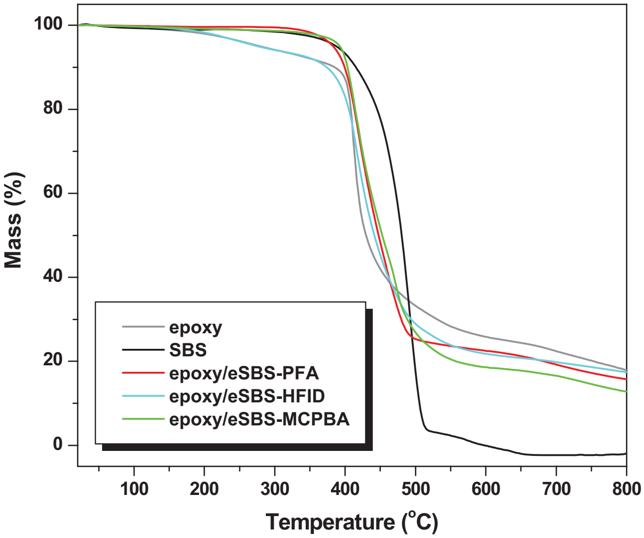


Figure 2.
The thermogravimetric analysis (TGA) plots of some of the blends compared with the pure epoxy resin and SBS copolymer; the blends were fabricated by using eSBS prepared *via* different methods (PFA, HFIP and MCPBA) as indicated.

remain no longer thermally stable above 180 °C. On the other hand, the block copolymer (pure SBS sample) begins to degrade at about 380 °C with the peak degradation temperature located at about 450 °C implying that the SBS sample is more stable than the resin. The residual mass after the TGA measurements was recorded after the completion of the experiment. It was found that about 16% of the total mass of the samples remained at the end of the experiment for epoxy resin and the blends studied while the mass of the eSBS sample was completely disappeared. The strong network structure of the epoxy resin and the blends might be the reason behind the formation of stable char which was not completely degraded under nitrogen atmosphere.

In the blends with eSBS prepared by different methods, the degradation temperature of the resin has shifted to much higher temperature (from 180°C in pure resin to approximately to 416 °C in the blend) except for the blend with eSBS prepared by HFIP method (in which the thermostability of the blend is similar to that of the pure resin). The addition of eSBS thus offers the possibility to increase, besides imparting an enhanced toughness, the thermostability of the materials. The improvement in thermostability of the materials might be correlated to the resulting nanostructured morphology of the blends.

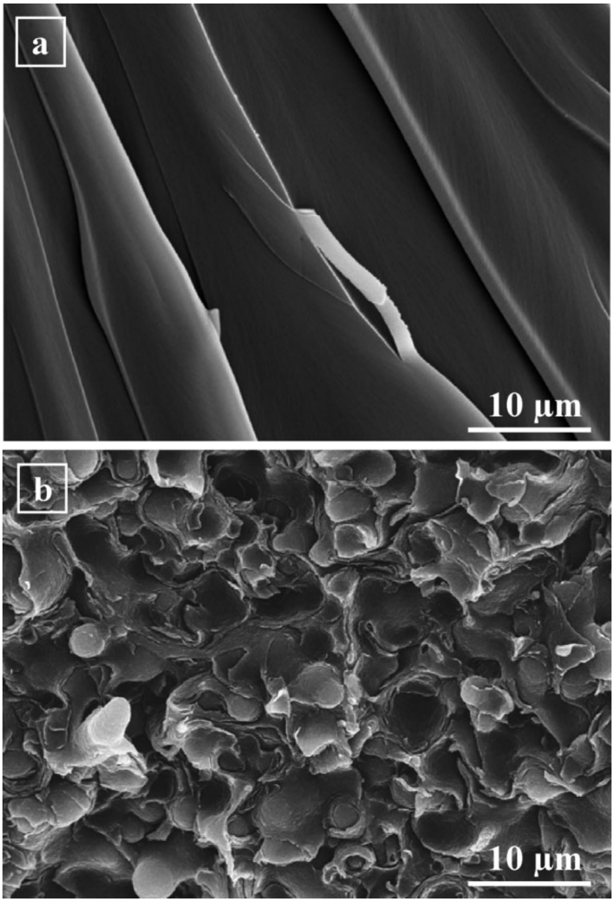


Figure 3.
SEM images of cryo-fracture surfaces of a) neat cured epoxy resin and, b) epoxy resin with eSBS (epoxy resin/eSBS blend ratio = 70/30); the eSBS copolymer was prepared by MCPBA method.

It is well known that chemical modification of any of the blocks of the block copolymer leads to a change in various properties of the polymer such as relative volume fraction of the components in the block copolymer, then the interaction parameter between the monomers and even molecular weight distribution and chemical architectures of the chains due to possible side reactions. Thus, looking closely at the FTIR results presented in Fig. 1, and recalling inferences of the TGA results presented in Fig. 2, we can deduce that microphase separation behavior of the resulting eSBS samples *via* different epoxidation routes may be drastically different. Hence, the properties of resulting blends may vary significantly. In the further discussion, we use the eSBS copolymer prepared by MCPBA method only.

Now, we analyze the fracture surface morphology of the cured pure epoxy resin and a blend with an epoxidized block copolymer (eSBS). The detailed nano-heterogeneous morphology of the samples will be reported in a future paper.[20] Here, we shed light on the effect of the addition of eSBS to the epoxy resin on the morphology of a selected blend. Fig. 3 compares the SEM micrographs of the typical fracture surface morphologies of pure epoxy resin with that of an epoxy/eSBS (70/30 by weight) blend.

The SEM image in Fig. 3a shows the fracture surface typical of a glass, i.e., with flat terraces formed by brittle failure of the materials; without any sign of fibrillation in the neat epoxy resin. The fracture surface of the pure epoxy resin implies that the resin is a capable material but breaks in a brittle manner. Now, the purpose of using the eSBS as a blend component was to modify the resin in such a way that the blend behaves in a ductile manner. For instance, Fig. 3b shows entirely different fracture surface morphology of the blend. The fracture surface morphology of the blend rather exhibits the typical matrix–particles morphology associated with intense plastic deformation and fibrillation of the matrix polymer typical of toughened plastic.[21] Thus, the structures observed on the fracture surface of the blend signify that the epoxy resin has been toughened significantly by the addition of the eSBS. The quantification of the toughness parameter is, nevertheless, not possible on the basis of available data.

Conclusion

A star shaped polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) block copolymer was successfully epoxidized *via* various methods using *m*-chloroperoxy benzoic acid (MCPBA), performic acid (PFA), peracetic acid (PAA) and hexafluoro isoprapanol (HFIP). All the methods were found to be basically suitable for the epoxidation of the styrene/butadiene block copolymer, among them, the HFIP method being the most time effective and the PFA the most cost effective ones. However, the eSBS samples modified by PFA and HFIP methods indicated the occurrence of rapid side reactions. For practical purposes, we found the MCPBA method as suitable means for the epoxidation of the styrene/butadiene block copolymers in terms of time, cost and ease of controlling reaction conditions. The addition of eSBS to the epoxy resin is found to offer the possibility of improving significantly the thermostability of the materials. The SEM analyses of the fracture surfaces of epoxy resin and a blend with eSBS show that the latter contributes significantly to improve the toughness of the resin. The effect of epoxidation degree of the copolymer and composition of the blend components on the morphology and deformation behavior of the blends are the objects of the ongoing studies.

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