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Morphological and Mechanical Characterization of Nanostructured Thermosets from Epoxy and Styrene-*block*-Butadiene-*block*-Styrene Triblock Copolymer

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ABSTRACT: Styrene-*block*-butadiene-*block*-styrene (SBS) triblock copolymers epoxidized at several epoxidation degrees by hydrogen peroxide in water/dichloroethane biphasic system were blended with epoxy based on diglycidyl ether of bisphenol A (DGEBA) and DDM (4,4'-diaminodiphenyl methane) as curing agent. The incorporation of epoxidized block copolymers in epoxy resulted in the formation of nanostructured blends. The morphologies of the blended polymers were studied using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS) analysis. The key factor controlling the morphology is the mole percentage of epoxidised butadiene units in SBS. In fact, the morphologies changed from macroscopic phase separated domains in unmodified SBS to nanostructured domains in epoxidised SBS and the resulting morphologies were fixed by the cross-linking reaction. Nanostructured morphologies such as worm-like and spherical micelles (radius 8 nm) were generated due to reaction induced phase separation of PS phase followed by the self-assembly of PB sub chains. The mechanical properties such as fracture toughness (stress field intensity factor (K_{IC})), and impact strength of these blended systems were measured. It was established that nanostructured blends significantly improved fracture toughness and impact strength. Field emission scanning electron micrographs of fractured surfaces were examined to understand the toughening mechanism.

INTRODUCTION

Thermosetting matrices like epoxy and novolac resins are used as high performance materials such as adhesives, matrices of composites, and coatings in the aerospace and electronic industries.^{1–3} Due to the highly cross-linked structure, they have drawbacks such as brittleness, poor resistance to crack propagation, and low impact strength. To improve the toughness of thermosetting matrices either elastomers or thermoplastic materials are added. Several studies have been done related to these fields.^{4–9} Uneffective compatibilization of thermoplastic mixtures (due to very high interfacial tension between the polymers) often gives poor mechanical properties of the blends in comparison with their components taken separately. Thus, in order to improve the compatibility, compatibilized block copolymers are added to the thermosetting matrices. The long-range ordered nanostructures are produced in epoxy matrix via self-assembling of amphiphilic block copolymers or by reaction induced phase separation, thus block copolymers act as the templates for the synthesis of nanostructures, hence the improvement in mechanical properties and toughness.^{10–22}

Recently researchers have been working on the fundamentals of structure–property relationship in nanostructured thermosets containing block copolymers. Improvements of maximum critical stress field intensity factors (i.e., K_{IC}) have been reported of around two times by particles forming the “sphere-on sphere” nanostructures in epoxy thermosets by Pascault et al.²³ Ritzenthaler et al. have modified DGEBA by blending with polystyrene-*block*-polybutadiene-*block*-poly (methyl methacrylate) (SBM) copolymer. The hardeners used were 4,4'-diaminodiphenyl sulfone (DDS) and 4,4'-methylenebis (3-chloro-2,6-diethylaniline) (MCDEA). Due to the formation of nanostructures before and after curing, the fracture toughness values enhanced when MCDEA was used as the hardener.^{24,25} Guo et al. carefully analyzed the fracture surface of nanostructured thermosets containing SSEBS-c-PCL and concluded that the improvement in toughness was caused by interfacial debonding of spherical microdomains, plastic void expansion,

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Table 1. Characteristics of Block Copolymers Used

block copolymer	degree of epoxidation ^a	polystyrene ^b (wt %)	polybutadiene ^b (wt %)	epoxidised PB ^b (wt %)	M _w ^c (g/mol)
SBS	0	31	69	0	150000
eSBS26	26	31	47	22	144700
eSBS39	39	31	35	34	145600
eSBS47	47	31	29	40	141300

^aMole percent of epoxidised polybutadiene units determined by the solid state ¹H NMR analysis. ^bWeight percent of polystyrene, polybutadiene, and epoxidized PB were obtained by solid state ¹H NMR analysis. ^cThe average molecular weight of block copolymers measured by GPC analysis.

and small scale matrix deformation.²⁶ However, toughening of the epoxy phase (macro phase) depends on several factors such as shape and size of the nanophase, interaction of the nanophase with the macrophase, debonding of micelles or vesicles (nano phase) from epoxy matrix, crack deflection, crack wave bridging, matrix shear banding induced by nanocavitation, etc.^{27–30}

The aim of this study was to investigate the effect of addition of poly (styrene-*block*-butadiene-*block*-styrene) (SBS) triblock copolymers on the morphology and mechanical properties of epoxy matrix cross-linked by 4,4'-diaminodiphenyl methane (DDM). More emphasis has been given to understand how the degree of epoxidation on the polybutadiene block in the triblock copolymer SBS influences the generation of nano-morphology and network structure of the epoxy system. In order for this, the PB block of the triblock copolymer has been epoxidized to different degrees to obtain morphologies of the epoxy/block copolymer in different length scales, from macroscale to nanoscale. Interestingly, spherical micelles and worm-like structures could be generated based on degree of epoxidation. The techniques used to characterize the morphology of the blends were scanning electron microscopy (SEM), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS) measurements. Mechanical properties such as impact strength and fracture toughness have been carefully evaluated. The mechanical properties have been carefully correlated with the generated morphology of the blends. Finally, the toughening mechanism of these blends has been discussed in detail. To the best of our knowledge, the role of eSBS on the morphology and mechanical properties of an epoxy (DGEBA) system cured with DDM has not been reported so far.

EXPERIMENTAL SECTION

Materials and Preparation of Samples. The epoxy resin used for this study was diglycidyl ether of bisphenol A (DGEBA), Araldite LY556 supplied by Huntsman with an average epoxy equivalent weight of 186 g/equiv. The used curing agent was 4,4'-diaminodiphenylmethane (DDM), supplied by Fluka. An amino hydrogen to epoxy stoichiometric ratio of one was selected for all the systems. The modifier was styrene-*block*-butadiene-*block*-styrene triblock copolymer (SBS) supplied by Kraton (KRATON D-1101) with weight average molecular weight of 150 000 g·mol⁻¹ and styrene weight percentage of 31 wt %. Tetrahydrofuran (99%) supplied by Sigma Aldrich was used as solvent.

To make effective the compatibilization of butadiene block in epoxy resin, epoxidation reactions were considered, with the aim of obtaining different epoxidation degrees by hydrogen peroxide in the presence of in situ prepared catalyst system in water/dichloroethane biphasic system. Selected articles were considered as reference papers for the epoxidation reaction.^{31,32} The different epoxidation degrees were obtained by varying the

time and temperature of epoxidation. The characterization of epoxidized block copolymer was done by means of solid state ¹H NMR and FTIR analysis. The epoxidised SBS (eSBS) was obtained at different epoxidation degrees. The epoxidation degree is the mole percent of epoxidised polybutadiene units, and it is measured by solid state ¹H NMR analysis. The characteristics of the epoxidized block copolymer at different epoxidation degrees are given in Table 1. The block copolymer used for this study were symbolized as SBS (styrene-*block*-butadiene-*block*-styrene) and eSBS (epoxidised SBS) with different degrees of epoxidation 26, 39, and 47 mol %.

The preparation of epoxy/SBS blends containing 10 wt % SBS with different epoxidation degrees was made by solvent casting method using tetrahydrofuran (THF) as solvent. For this purpose, the block copolymer and epoxy resin were dissolved in THF until a homogeneous mixture was obtained, the mixture was heated at 80 °C in an oil bath for the complete removal of the solvent. After the removal of the solvent, the temperature was increased up to 90 °C and a stoichiometric amount of the hardener DDM was added. The components were mechanically mixed for 5 to 10 min using a magnetic stirrer. Then the mixture was poured into a silicon mold and kept in a vacuum oven for 24 h for the removal of air bubbles and the remaining solvents. The blends were cured at 50 °C for 2 h, 80 °C for 3 h, and 140 °C for 3 h in an oven and then allowed to cool the samples slowly to room temperature.

Characterization Methods. *Differential Scanning Calorimetry (DSC).* The glass transition temperature (*T*_g) of SBS and eSBS was analyzed using TA Q200 differential scanning calorimeter. Samples of about 5–10 mg were placed in aluminum pans and heated from –100 to 50 °C at the heating rate of 10 °C/min.

Field Emission Scanning Electron Microscopy (FESEM). The morphology of the fractured surface of cross-linked epoxy and epoxy block copolymer blends were examined at an accelerating voltage of 15 kV using a ULTRA FESEM, (model - ultra plus) Nano Technology Systems Division Carl Zeiss SMT AG, Germany. The fractured samples were prepared at room temperature and then coated with platinum by vapor deposition using a SCD 500 Sputter Coater (BAL-TEC AG, Liechtenstein) before analysis.

Transmission Electron Microscopy (TEM). TEM images were obtained with a JEOL JEM –2100 microscope applying an acceleration voltage of 100 kV in bright field and dark field mode. The specimens were prepared using LEICA Ultracut ultramicrotome. Thin sections of about 70 nm were obtained with a diamond knife at room temperature and deposited on copper grids.

Small Angle X-ray Scattering (SAXS). The SAXS patterns of the samples were recorded by a MBraun system, using a Cu K α radiation (1.5418 Å) from a Philips PW 1830 X-ray generator. The data were collected by a position sensitive detector and

were successively corrected for blank scattering, desmeared, and Lorentz-corrected. Collecting time was 1800 s.

Impact Tests. Izod bars were notched and tested at ambient conditions according to the ASTM D 256 method. Impact loading was done with a 25 J-hammer. For each blend at least five samples were tested and their results were averaged. The sample dimensions were 64 mm × 12.7 mm × 4 mm.

Fracture Toughness Measurements. Fracture toughness was measured by the single edge notched three-point bending test using Lloyd instrument LR30K universal testing machine according to ASTM D-5045 standard. A crosshead speed of 10 mm/min was used. The critical stress intensity factors (K_{IC}) were calculated using the following equation:

$$K_{IC} = (F_{max}/BW^{1/2})f(a/W) \quad (1)$$

where F_{max} is the maximum load at failure, B is the thickness of the specimens, W is the width of the specimens, a is the crack length, and $f(a/W)$ is the expression accounting for the geometry of the sample. The expression for $f(a/W)$ is given in ASTM standard D-5045. Central Vee-notches were machined. Subsequently, a razor-sharp crack tip was initiated with a fresh razor blade. At least five successful measurements were used to obtain the average values of experiments. The samples were parallelepipedic bars of 35 mm × 8 mm × 4 mm and the notch being around 4 mm.

RESULTS AND DISCUSSION

Optical Clarity and Initial Miscibility by T_g Analysis.

The visual study about the transparency of the system (Figure 1) shows that the epoxy mixture containing unmodified SBS is

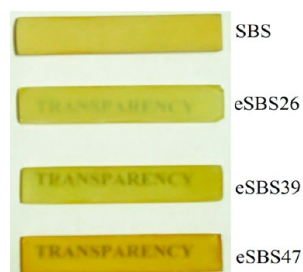


Figure 1. Digital camera images of 10 wt % of SBS modified epoxy/DDM blends (with different epoxidation degrees).

opaque, confirming heterogeneous morphology and macroscopic phase separation. The one which is epoxidised at low epoxidation degrees (eSBS26) is initially heterogeneous and found to be translucent after the curing reaction. It is visualized that blends of epoxy with eSBS39 were initially miscible and become translucent after the curing reaction. At high epoxidation degrees, eSBS47, the obtained blends are transparent before and after the curing process, showing the good compatibility with epoxy resin matrix. This may be due to the fact that the size of the particles in the epoxy matrix decreases from the macro level to micro and then to the nano level. Hence, when the epoxidation degree is 26 mol %, this amount of epoxidation degree was not enough to produce nanostructures in epoxy matrix. Further studies were done using FESEM, TEM, and SAXS measurements and the specific results confirmed this initial observation. The initial miscibility showed that there could be secondary interactions (i.e., hydrogen bonding) between the hydroxyl group of the growing epoxy thermoset and epoxy groups of the epoxidized butadiene.

These interactions are more pronounced in the case of blends with highest epoxidation degrees, and hence, there is a chance of increase in miscibility or compatibility as the epoxidation degree increases.³³ Recently, we have also recognized that epoxy/amine reaction rate was reduced by the addition of eSBS. Moreover, epoxidized SBS and unmodified SBS have limited reactivity or no reactivity with [NH] group in DDM; that means DDM has been completely used for the curing of DGEBA.³³

The T_g values of PB block in epoxidised SBS were measured by differential scanning calorimeter (DSC) and these values were found to increase with the epoxidation degree (Table 2).

Table 2. T_g Values of Neat and Epoxidized SBS at Different Epoxidation Degrees

epoxy/eSBS/DDM (10 wt %)	T_g of PB (°C)
SBS	−87
eSBS (26 mol %)	−60
eSBS (39 mol %)	−43
eSBS (47 mol %)	−38

The increase in values of T_g for PB in epoxidised SBS gives the information about the polarity of the PB phase, because epoxidation results in a systematic increase in polarity and miscibility butadiene units in epoxy matrix.³⁴

Phase Morphology of Epoxy Blends. The morphology (fracture surface) of cured blends was studied using FESEM. Figure 2a shows the SEM micrographs of the neat epoxy system, which reveals a single phase. The fracture surface was typically flat and smooth and the cracks spread freely and regularly and orient in the direction of the loading, typical for a brittle material. For the blends containing unmodified SBS that is with 0 mol % epoxidation degree a heterogeneous morphology with phase separated structure is observed (Figure 2b). The figure (Figure 2b) specifies that the phase separation occurs in the macroscopic length scale. The styrene and butadiene domains are coagulated in the epoxy matrix. Figure 2c shows the sample with the lowest degree of epoxidation eSBS26, which has a better compatibility of block copolymer in the epoxy matrix due to the epoxidation of butadiene and in which the size of the immiscible domain is decreased. As the epoxidation degree increases, the heterogeneous morphology changes to homogeneous morphology. It can be seen that when the epoxidation degree reaches 39 mol %, (Figure 2d, e, and f) the domain size of the block copolymers in epoxy matrix again decreases and form domains in the size of nanometer scale. On the other hand, for 47 mol % epoxidation, (Figure 2g and h) the blend surface looks homogeneous, but the magnified image (Figure 2i) reveals PS nano phase; however, these are too small. It is difficult to find out the exact morphologies of the blends with 39 and 47 mol % epoxidized SBS by SEM images. However, it can be concluded that there is a change in morphology from macroscopic level to nanolevel (Figure 2). Or in other words, epoxidized copolymers at highest degree of epoxidation could be able to create nanostructured templates in epoxy resins.

TEM investigations were made for selected samples to provide supporting evidence to the above results obtained by SEM. TEM is an excellent tool to find the various ordered and disordered morphologies in the cured blends as the epoxy concentration varies.^{35,36} TEM micrographs were recorded for the blends containing 10 wt % of eSBS epoxidized at different

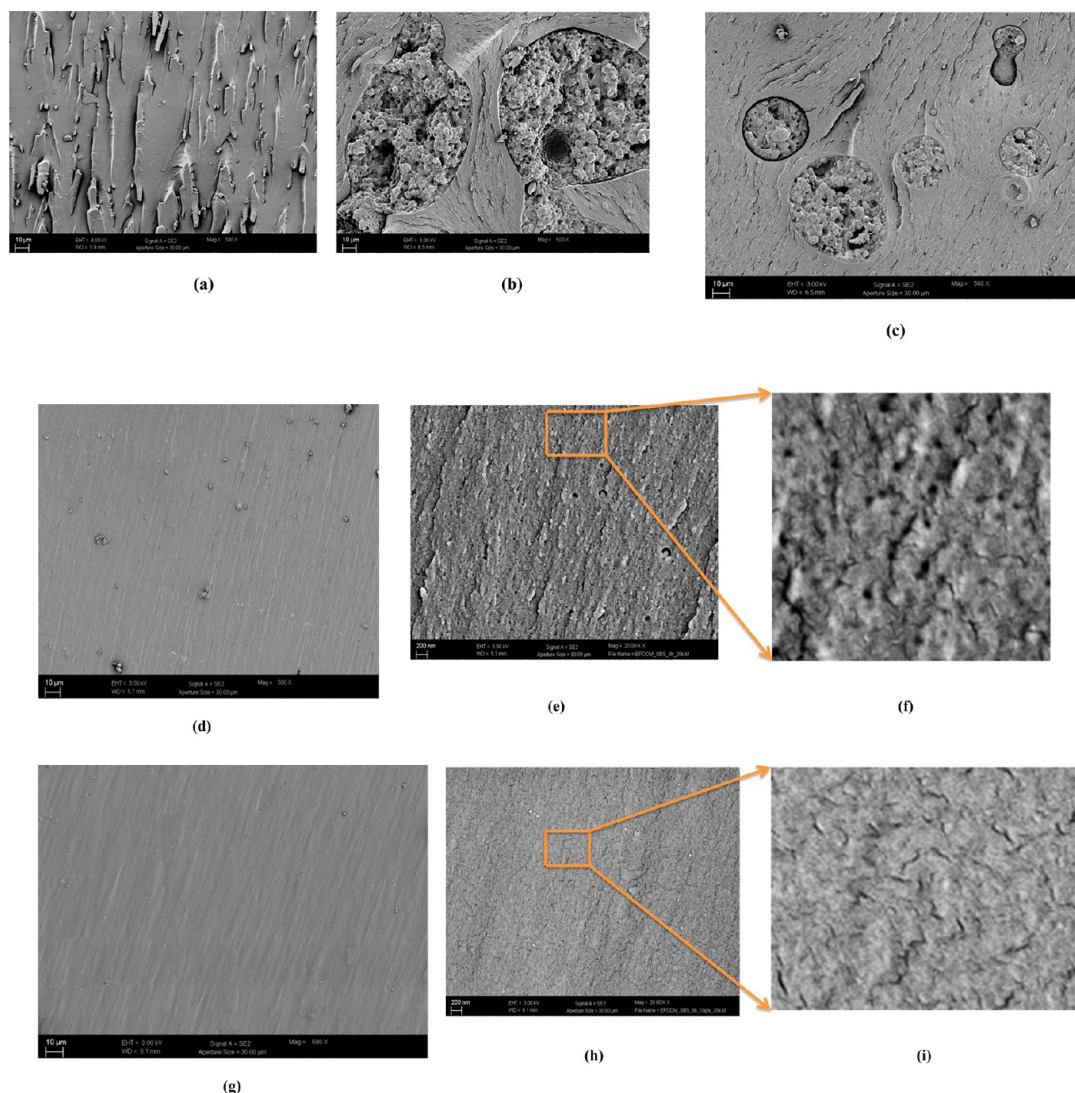


Figure 2. SEM micrographs of fracture surface of (a) neat epoxy, (b) epoxy blends with 10 wt % SBS, (c) epoxy blends with 10 wt % eSBS26, (d, e, and f) epoxy blends with 10 wt % eSBS39 ((f) high magnification ($1000 \times 800 \text{ nm}^2$)), (g, h, and i) epoxy blends with 10 wt % eSBS47 ((i) high magnification ($800 \times 600 \text{ nm}^2$)).

epoxidation degrees 39 and 47 mol %. Figure 3a and 3c are the TEM images of epoxy matrix containing eSBS at highest degrees of epoxidation (eSBS39 and eSBS47) showing nanostructure with phase separation in the nanometer range. Due of the difference in electron density of different groups, the bright continuous areas can be ascribed to cross-linked epoxy matrix.³⁷ This means that, the continuous phase is the epoxy phase in which eSBS block copolymers are dispersed.

For the epoxy blends with eSBS39, worm-like micelle with an average diameter of around 20–30 nm in size are dispersed in the epoxy matrix. In addition, owing to the diversity in the preference of RuO_4 staining, dark outer layers of worm-like micelles can be attributed to the unepoxidized PB phase, whereas the bright inner core can be assigned to the phase-separated polystyrene (PS) blocks, as illustrated in Figure 3a.^{37–40} The reduced compatibility of epoxidized PB blocks in epoxy matrix is due to the presence of unepoxidized PB block, that produces a tendency toward aggregation of vesicles and hence a worm-like micelle morphology. Figure 3b reveals a schematic representation of epoxy/eSBS39 blends with worm-like micelle, shows an outer layer of unepoxidized PB and an

inner layer of PS blocks. Once the epoxidation degree reaches 47 mol %, these interconnected worm-like micelle morphologies are changed to long-range ordered nanostructured spherical micelles with an average diameter of around 10–20 nm in size, which are dispersed continuously in the epoxy matrix (Figure 3c). The weight percentage of epoxidized PB reaches 40 at epoxidation degrees 47 mol %. As a consequence long-range ordered nanostructures are formed. Thus the compatibility of block copolymer increases with the epoxidation degree and hence the transparency also. Figure 3d reveals a schematic representation of DGEBA/eSBS47 blends with spherical micelles. The spherical micelles consist of outer layers of unepoxidized PB and the inner core of PS, which are dispersed in the thermosetting matrix.⁴¹

Mechanism of Phase Separation. As mentioned in the introduction thermoplastic containing amphiphilic block copolymers phase separate through two mechanisms, self-assembly and reaction induced phase separation depending on the miscibility of the subchains of the block copolymer before and after curing reaction. Since PB subchains remain immiscible in the epoxy resin, one should expect the formation

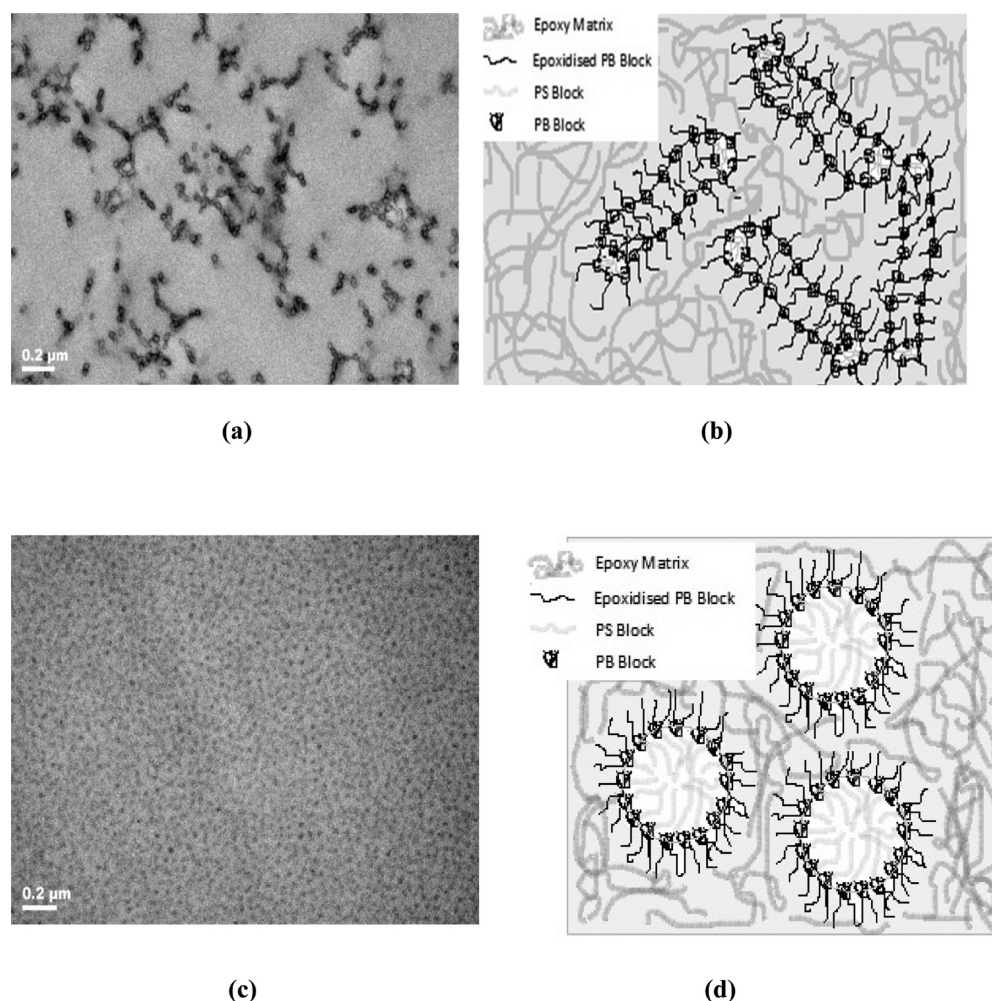


Figure 3. TEM images of epoxy/eSBS/DDM blends containing 10 wt % eSBS epoxidized at (a) 39 and (c) 47 mol %, schematic representation of epoxy/eSBS/DDM blends containing 10 wt % eSBS epoxidized at (b) 39 and (d) 47 mol %.

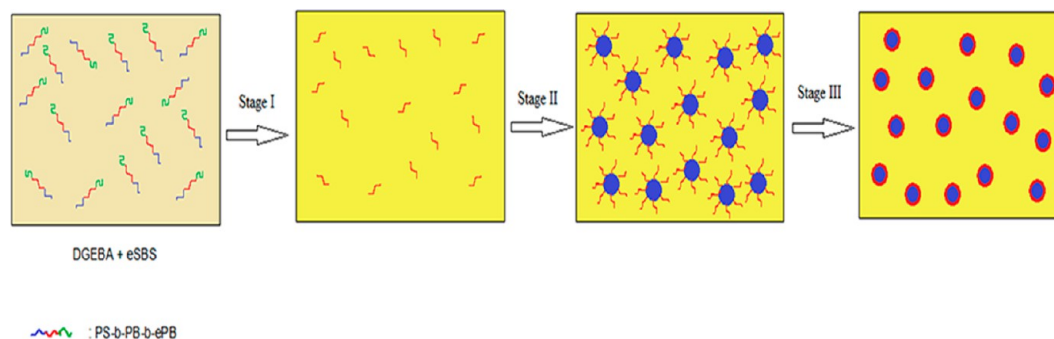


Figure 4. Formation of nanostructures in epoxy thermosets and demixing of PS blocks out of epoxy-amine matrix.

of PB core by self-assembly before curing followed by reaction induced phase separation of PS phase over the PB phase as indicated by Ocando et al.⁴² But this is not true in every case; we have initially small unepoxidized PB phase present in the homogeneous DGEBA/eSBS mixture. However up on epoxy/amine curing a part of the PS subchain may phase separate to form nanosized PS core, followed by reaction induced self-assembly of most of the unepoxidized PB phase to form a shell of PB chains over the PS core. The driving force for the segregation of PB chains at the interface between the PS and epoxy continuous phases is the minimization of the specific

interfacial energy of the system.⁴³ A schematic model describing the evolution of phase separation based on FESEM and TEM micrographs are given in Figure 4. Stage I in Figure 4 represents the immiscible PB phase in a homogeneous epoxy/eSBS mixture. In stage II, nucleation and growth mechanism (NG) initiated by reaction induced phase separation is depicted, which results in PS particles, followed by the self-assembly of PB phase on the surface of the PS particles, this is because the nonpolar PB phase has more affinity toward the nonpolar PS particles. In stage III, the PB phase forms a layer around the PS particles. It is important to

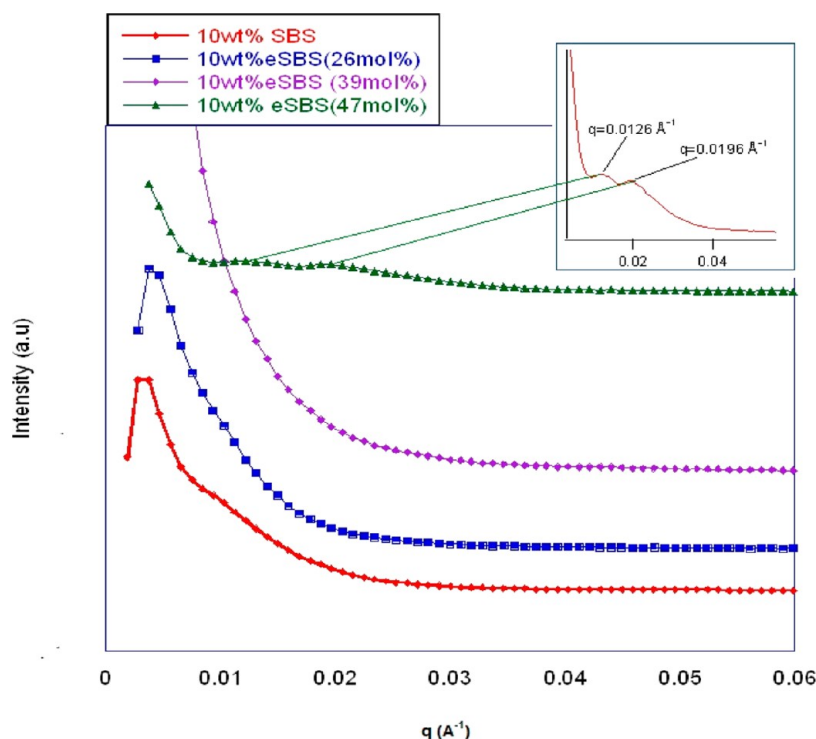


Figure 5. SAXS patterns of DGEBA/eSBS/DDM blends at room temperature (25 °C) with different epoxidation degrees (q is the scattering vector).

add that most of the epoxidised PB chains may get completely extended into the epoxy matrix due to the hydrogen bonding interaction between the hydroxyl groups of the growing epoxy thermosets and the epoxy groups of the epoxidised block of PB subchains.³³

Small Angle X-ray Scattering (SAXS). The morphology of cured blends with 10 wt % of the copolymer at different epoxidation degrees were investigated by SAXS technique. The SAXS profiles are shown in Figure 5. Well-defined scattering peaks were observed only in the case of the blend with highest epoxidation degree (eSBS47), indicating that in such cases an ordered microphase-separation occurred. The SAXS patterns of samples 10 wt % SBS, 10 wt % eSBS (26 mol %), and eSBS (39 mol %) showed a shoulder in the region between 0.01 and 0.02 \AA^{-1} , i.e. in the region where the first peak appeared for 10 wt % eSBS (47%). This is indicative of a correlation between the microdomains formed in these copolymers. However, the absence of well-defined scattering peaks and especially of higher-order signals reflects a lower regularity in the microphase separation in these materials.

According to the position of the primary scattering peak, the average distance between neighboring domains can be estimated to be 61 nm for the thermosets containing eSBS47 block copolymer. The relative peak position observed in the SAXS pattern for the highest epoxidation degree is 1:1.55. The most common morphologies of phase separation, i.e. lamellar, body centered cubic lattice of spheres, hexagonal lattice of cylinders, would predict the second order peak at a relative position of 2, $\sqrt{2}$, and $\sqrt{3}$, respectively. None of these expected positions correspond to the experimentally determined, which is halfway between $\sqrt{2}$ and $\sqrt{3}$. In addition to this, the absence of further higher order peaks does not allow to solve this ambiguity, so a precise attribution of the morphology of microphase separation is not possible only by SAXS. However, SAXS results are in a good agreement with the

conclusions obtained by means of TEM. As noted by microscopy techniques, sample eSBS47 is the only one displaying a regular domain separation in the length scale of the nanometers. On the other hand, the samples with a lower epoxidation degree are characterized by a less regular microphase separation, and as a consequence in SAXS they yielded almost featureless patterns, with just a weak shoulder. This seems to be related to the increase in compatibility between the epoxidized block copolymer and the epoxy system.^{44–46}

Mechanical Properties. Impact Strength. For the DGEBA/eSBS/DDM blends, a significant increase of notched impact strength was in fact obtained with respect to the neat matrix. Figure 6 shows the impact strength of the 10 wt % of DGEBA/eSBS/DDM blends with different epoxidation degrees. From the figure, it is found that, compared to neat epoxy system, as the epoxidation degree increases, the impact strength also increases. Nearly 100% increase in impact strength occurs when the epoxidation degree reaches 47 mol %. Impact energy of blends with unmodified SBS is found to be low when compared to neat cross-linked epoxy. This is most likely due to the incompatibility of block copolymers in epoxy matrix. If there is no epoxidation of butadiene in SBS, the self-assembling of block copolymers in epoxy matrix does not occur. This self-assembling of block copolymers in thermosetting matrix occurs when the degree of epoxidation reaches a maximum value (eSBS47), and we observe uniformly dispersed spherical micelles of PS domains. This ordered arrangement of PS domains results in the increase in impact strength of epoxy blends with highest epoxidation degree.

Fracture Toughness. Figure 7 shows the fracture toughness values of epoxy system modified with block copolymer at different epoxidation. The fracture toughness values, or critical stress intensity factor, of epoxidised SBS blends increase gradually with the degree of epoxidation, but compared to neat

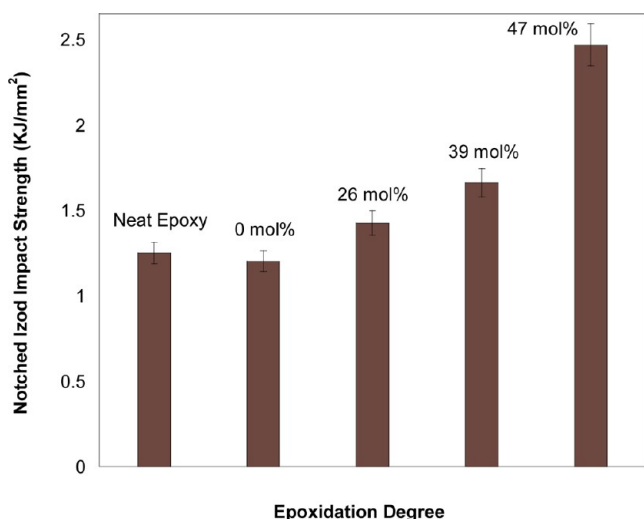


Figure 6. Notched Izod impact strength of 10 wt % DGEBA/eSBS/DDM blends with different epoxidation degrees.

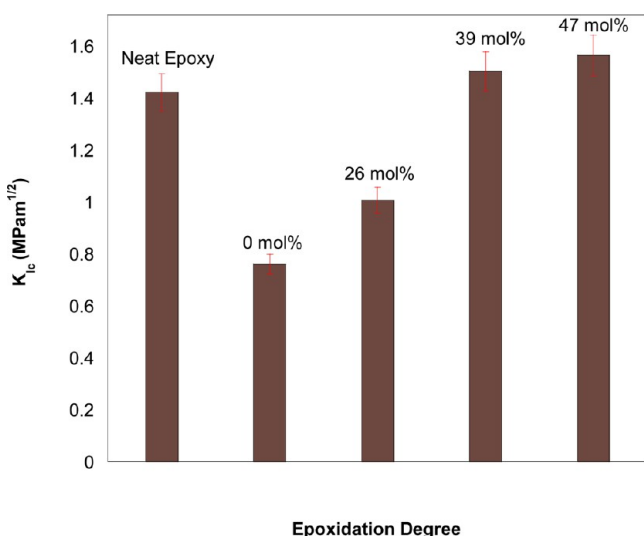


Figure 7. Fracture toughness values of DGEBA/DDM blends contacting eSBS at different epoxidation degrees.

epoxy system, this increase is not very high. Ocampo et al. have already reported that the fracture toughness value of neat epoxy system is increased with the epoxidised C500 block copolymer system.⁴⁷ Considering the blends with unmodified SBS, the fracture toughness value is much lowered. The critical stress intensity value of neat epoxy system is 1.4 MPa m^{1/2}, and this value is reduced to 0.8 MPa m^{1/2} for the blends with unmodified SBS. The reason for reduction in fracture toughness is mainly due to the phase separation of styrene and butadiene domains in macroscopic level and the poor interfacial interactions between the epoxy matrix and the phase separated domains. In the case of blends with low epoxidation degree i.e., with eSBS26, the toughness value (1 MPa m^{1/2}) is again low compared to neat cross-linked epoxy. The macro to nano level morphology changes caused a significant enhancement in toughness. At high epoxidation degree, say eSBS47 the toughness value is 1.6 MPa m^{1/2} higher than the neat epoxy matrix due to the self-assembling of block copolymers in nanoscale and the plasticization of epoxidised polybutadiene units in the epoxy matrix. Similarly other studies also reveal

significant improvement in epoxy matrix toughness by the addition of block copolymers.^{35,48,49}

The toughness improvement in epoxy blends with liquid rubber has been extensively studied for the last few decades. The main mechanism for the improvement in toughness is due to rubber cavitation, shear yielding, particle bridging, tearing of rubber particles, etc.^{4,50–52} On the other hand, the mechanism for toughness improvement in epoxy blends with block copolymers containing rubber phase has not been completely explored yet. Figure 2 reveals the fracture surface of epoxy blends with block copolymers. It was observed that fracture surface of epoxy blends with degree of epoxidation 39 and 47 mol % (Figure 2d and g) are smooth, even without fractures especially for epoxy blends with degree of epoxidation 47 mol %. A careful examination of 39 mol % blend reveals nanodomains or nanocavities, uniformly dispersed (Figure 2f). The micrograph reveals the existence of tiny cracks, along the main crack growth direction, and these cracks are pinned by the nanodomains. It is important to add that the fracture surface is similar to that of a ductile material due to the plasticizing effect of epoxidised PB phase. On the other hand, nanodomains are too small, from the magnified images of 47 mol % blend (Figure 2i). This is due to hydrogen bonding interactions between the hydroxyl group of the growing epoxy thermoset and epoxy groups of the epoxidized butadiene.³³ These interactions are more pronounced in the case of blends with highest epoxidation degrees and hence better adhesion between the matrix and nanodispersed block copolymer domains. Therefore, the load applied is transferred more effectively to the nanostructured domains from the cross-linked epoxy phase.⁵³ From the SEM micrographs of 47 mol % blend, nanocracks were observed in all directions and are deviated from its original plane, resulting in an increased surface area of the crack, which may increase the toughness.^{6,54} Another important parameter influencing the fracture toughness is the domain size. The domain size influences the efficiency of the initiation of energy absorbing mechanisms. Hence, the smaller domains in 47 mol % blend containing blends are effective in initiating energy absorbing mechanisms in comparison with other blends with larger domains. Moreover the domains are uniformly dispersed in the thermosetting matrix which will greatly optimize the interactions between the thermosetting matrix and the modifier.⁴⁸ The improvement in fracture toughness in epoxy/eSBS blend system could also be related to the decrease in cross-linking density of thermoset matrix owing to the dilution effect imparted by the eSBS subchains.⁵⁵ It is important to mention that many nanocavities are observed in the fracture surface, the energy-dissipation mechanisms could also be related to the formation of plastic shearing deformation induced by the nanocavitation of eSBS nanodomains in the nanostructured epoxy thermosets.⁵⁶ Thus the increase in fracture toughness of the epoxy/block copolymer blend system is due to the combined effect of different phenomenon taking place in the matrix during the application of applied load.

CONCLUSION

The epoxidation reaction in SBS influences the compatibility of block copolymer in epoxy matrix and also in the toughness of epoxy matrix. The epoxidation of triblock copolymer is carried out at different epoxidation degrees and illustrates a good compatibility at highest epoxidation degree i.e., at 47 mol %. The improvement in compatibility changes the morphology and mechanical properties. The nanostructured morphologies

obtained from field emission scanning electron microscopic (FESEM) analysis at high epoxidation degrees are confirmed by high resolution transmission electron microscopy (HR-TEM) and small-angle X-ray scattering (SAXS). Spherical micelle-like morphologies are obtained when the epoxidation degree is 47 mol %. The spherical micelle-like morphology changes to elongated vesicle-like domains in the blends with 39 mol % of epoxidation. The formation of the nanostructures in the thermosetting composites was judged to follow reaction-induced microphase separation and then self-assembly in terms of the difference in miscibility of epoxidized poly-(butadiene) and poly(styrene) sub chains with epoxy system after and before curing reaction. The fracture toughness of the epoxy thermoset was significantly improved by the inclusion of a small amount of eSBS triblock copolymer.

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Notes

The authors declare no competing financial interest.

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