Nanostructured Thermosetting Systems by Modification with Epoxidized Styrene−Butadiene Star Block Copolymers. Effect of Epoxidation Degree

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ABSTRACT: Novel epoxy-based blends containing 30 wt % star styrene-*b*-butadiene block copolymers epoxidized at several degrees (SepB) have been investigated in order to analyze the effect of epoxidation degree on the ability of these copolymers to produce nanostructures inside the epoxy matrix as well as their effect on the network structure of the matrix. For neat styrene−butadiene (SB) and SepB15-modified systems, macroscopic phase separation was observed. The SepB epoxidized at 40−76 mol %, however, yielded hexagonally ordered nanostructures formed by PS cylinders arranged in the matrix containing also the epoxidized and nonepoxidized butadiene units. DSC analysis indicates that the slight differences observed in self-assembling of the mixture containing the 40 wt % epoxidized block copolymer with respect to those for the blends with higher epoxidation degrees could be related with reactivity differences of the epoxidized copolymers with the curing agent. It is envisaged that these novel nanostructured blends may lead to novel materials with excellent optical properties and enhanced fracture toughness.

Introduction

Block copolymers (BC) are the focus of a great deal of research activity because of their intrinsic ability to self-assemble into different nanoscale structures. This intriguing ability can be used to design new polymeric nanostructures with potentially interesting properties. As has been reported by several authors, self-assembling of BC can be maintained in their blends with several homopolymers.[1−5] In this way, block copolymers are widely used as templates for generating nanostructured epoxy or phenolic matrixes with long-range order in both uncured and cured states.[6−18] One feasible pathway for generating self-assembled thermosetting nanostructures is the use of amphiphilic block copolymers, with one of the blocks miscible with the epoxy resin.

Hillmyer et al.[7,8] reported the first nanostructured system obtained by modification of a network-forming formulation composed of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin and an aromatic amine with amphiphilic diblock copolymers such as poly(ethylene oxide)-*block*-poly(ethylethylene) (PEO−PEE) and poly(ethylene oxide)-*block*-poly(ethylene-*alt*-propylene) (PEO−PEP). Before curing, epoxy resin swells PEO chains, leading to a morphological behavior similar to those corresponding to nanoordered homopolymer/block copolymer blends. After curing, the nanostructures were retained and cure-induced phase transitions occurred because of the local expulsion of PEO chains from the epoxy matrix. Afterward, several works have been reported describing nanostructured thermosetting materials by modification of epoxy resins with PEO-based block copolymers.[9−11]

Ritzenthaler et al.,[12,13] on the other hand, blended polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) copolymer with DGEBA by using 4,4′-diaminodiphenyl sulfone (DDS) and 4,4’-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) as hardeners. By using MCDEA, different nanoordered morphologies were obtained before and after curing, showing an enhancement on fracture toughness of the epoxy matrix. They found that the requirement to obtain nanostructured thermosets with SBM triblocks copolymers is the solubility of the corresponding PMMA block with the growing thermoset during the whole reaction.

A second generation of block copolymers has been developed for using the concept of chemical compatibilization. This approach incorporates reactive groups into one block in order to promote covalent bonding with the forming epoxy network without loss of ordering in the resulting blends.[6,16−19] This pathway could lead to an improvement in mechanical properties (notably fracture toughness) and in the stability of nanostructured materials.[16−18] Copolymers based in glycidyl methacrylate[16,18] and methacrylic acid[17] have been used by several authors. Rebizant et al.[16] obtained nanostructured thermosets, via DGEBA/DDS, by using polystyrene-*block*-polybutadiene-*block*-poly(glycidyl methacrylate) (SBGM) copolymers instead of the analogue SBM triblock copolymer, which macrophase-separates. Similar results were obtained by Grubbs et al.[18] with a polyisoprene-*block*-poly(methyl acrylate-*co*-glycidyl acrylate) (MG-I) copolymer by using 4,4′-methylenedianiline (MDA) as hardener.

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Reactive rubbers have been widely used as modifiers of epoxy systems. The aim of these modifications is to toughen the very brittle epoxide network with a rubbery dispersed phase.[20−22] In this sense, epoxidized natural rubber is also an excellent alternative to toughen epoxy resins because of its good reactivity and acceptable compatibility with the epoxy matrix.[22,23] Hon et al.[23] studied the effects of epoxidized natural rubbers on mechanical properties of epoxy-cured macroseparated systems, finding a better toughness for modified systems without loss of stiffness. However, even though reactive rubber is a good modifier, certain properties of the epoxy matrix suffer from its addition. In particular, the optical transparency of the matrix is lost after the addition of the rubber modifiers, and stiffness of the matrix is reduced but no mechanical properties. Grubbs et al.,[18,19] on the other hand, synthesized reactive poly(epoxyisoprene)-*block*-polybutadiene copolymers, obtaining nanostructured thermosets with epoxy/MDA systems for high copolymer contents and an increase of improvement of fracture toughness of the epoxy resin for low-copolymer contents. Epoxidation of styrene−butadiene (SB) block copolymers has been the pursued goal of several groups for different applications such as adhesives, etc.[24−26] In the present study, we have focused on epoxidizing a commercial star block SB copolymer and use this to obtain nanostructured thermosetting materials of the epoxy matrix.[27] The reason for choosing a star block copolymer is twofold: first, we were interested in investigating the effect of architecture on the nanostructuring of the epoxy matrix, and to the best of our knowledge, until today, no one has investigated star block copolymer modifiers for epoxy matrixes, and second, we wanted to use a commercially available material with relatively low cost because most of the literature deals with custom-made block copolymers. The chosen block copolymer system conforms to both of these requirements. It should be noted that, quite obviously for potential applications, the developed systems must be cheap and commercially available.

Recently, we have reported preliminary results for a systematic method for the preparation of a nanostructured epoxy system modified by an epoxidized SB star block copolymer containing 61 mol % epoxidized butadiene units.[28] The aim of the present work is to systematically study the effect of epoxidation degree in the ability of block copolymers to form nanoordered thermosetting materials. In this context, the morphological and dynamic-mechanical behavior of DGEBA/MCDEA cured blends containing 30 wt % block copolymers epoxidized at several degrees as compared with the epoxy matrix modified with neat SB block copolymer have been analyzed.

Experimental Section

Materials. *Epoxidized SB Star Block Copolymers*. The copolymers used were styrene−butadiene block copolymers epoxidized at several degrees, SepB, obtained by epoxidation of a commercial SB star block copolymer, Kraton D-4272 CS (58.5 wt % PS, 3.9 wt % 1,2-PB, and 37.6 wt % 1,4-PB). The epoxidation reaction was carried out by using hydrogen peroxide in the presence of an in situ prepared catalyst system in a water/dichloroethane biphasic system. This epoxidation reaction procedure leads to mainly 1,4-epoxidized butadiene units. The details of the reaction are described in detail elsewhere.[27] Throughout the present study, the commercial copolymer is denoted SB, and the epoxidized copolymers are denoted SepB*x*, where *x* symbolizes the degree of epoxidation. The characteristics of the copolymers used are listed in Table 1. It should be mentioned that weight and number-average molecular weights have been estimated from ^{1}H nuclear magnetic resonance (^{1}H NMR) measurements and by assuming the same polydispersity as that for SB copolymer.[29]

Table 1. Characteristics of the Copolymers Used

block copolymer designation	epoxidation degree[a]	S[b] (wt %)	B[c] (wt %)	EP[d] (wt %)	M_w[e] (g/mol)	M_n[e] (g/mol)
SB		58.5	41.5	0	245 000[f]	183 000[f]
SepB15	15	57.5	34.6	7.9	250 000	186 600
SepB40	40	55.8	23.7	20.5	256 000	191 000
SepB61	61	54.5	15	30.5	263 000	196 300
SepB76	76	53.6	9.5	37	268 000	200 000

[a] Defined as mol % of epoxidized polybutadiene units and determined by ^{1}H NMR analysis. [b] Polystyrene, as determined by ^{1}H NMR analysis. [c] Polybutadiene, as determined by ^{1}H NMR analysis. [d] Epoxidized polybutadiene units, as determined by ^{1}H NMR analysis. [e] As described in Experimental Section. [f] From GPC measurements.

Thermoset Precursors. The epoxy monomer used, DER 332, was a diglycidyl ether of bisphenol A, kindly supplied by Dow Chemical. It has an epoxy equivalent of around 175 and an average number of hydroxyl groups per two epoxy groups $n = 0.03$. The hardener used was an aromatic diamine, MCDEA, from Lonza. The characteristics and structures are listed in Table 2. The epoxy monomer and the diamine were used in an amino-hydrogen-to-epoxy stoichiometric ratio equal to 1.

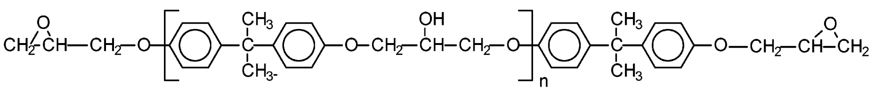
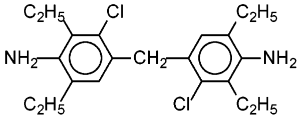
Blending Protocol. Copolymer/epoxy systems were cured in the following way: first, the copolymer and the DGEBA resin were dissolved in tetrahydrofuran (THF). The resultant solution was heated at 80 °C in an oil bath until complete solvent removal was obtained. Then the temperature was raised to 140 °C, and MCDEA was added to the sample. As reported for SepB61-modified system,[28] after THF evaporation, block copolymers were partially miscible with uncured epoxy resin, even after addition of MCDEA, due to partial miscibility of both PS block and epoxidized PB segments. The samples were degassed in a vacuum and cured at 140 °C during 24 h. Finally, the samples were postcured at 165 °C for 2 h.

Dynamic Mechanical Analysis (DMA). DMA analysis was carried out on cured blends with a Perkin-Elmer DMA7 in a three-point bending mode in order to obtain dynamic mechanical spectra (storage modulus, E', and loss factor, tan δ) between -120 and 210 °C. The scans were carried out at a frequency of 1 Hz and a heating rate of 5 °C/min, using a span of 15 or 5 mm for the low- and high-temperature range, respectively. The samples used were parallelepiped bars ($24 \times 3 \times 1$ mm^3). During the scans, the samples were subject to a static force of 110 mN and a dynamic force of 100 mN.

Morphological Analysis. The morphological features of the cured blends were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). AFM images were obtained operating in soft tapping mode with a scanning probe microscope (Nanoscope IIIa, Multimode from Digital Instruments) equipped with an integrated phosphorus doped tip/cantilever having a resonance frequency ∼180 kHz, from the same manufacturer. The height and phase images were obtained under ambient conditions with typical scan speeds of 0.5−1 line/s, using a scan head with a maximum range of 16 μm × 16 μm. A Hitachi H-800-MT microscope, operated at 100 kV accelerating voltage, was used for TEM measurements. Samples of SepB15-modified systems for AFM observations were prepared by cryogenic fracture. On the other hand, both AFM and TEM samples of blends containing higher epoxidized copolymers were prepared by using an ultramicrotome (Leica Ultracut R) equipped with a diamond knife. The samples were stained with OsO_4 vapor for 4 min for TEM observations to enhance contrast between the PB and PS/epoxy regions.

Small-Angle X-ray Scattering (SAXS). SAXS measurements were carried out in transmission geometry on a three-pinhole collimated system equipped with a Rigaku rotating anode (Cu Kα radiation $\lambda = 1.542$ Å, operating at 4.2 kW), an Osmic multilayer mirror for higher photon flux, and a MARCCD 2D detector (average pixel size 78.7 μm × 78.7 μm). The sample-to-detector distance was 1.8 m, and it was calibrated by using Ag−Behenate as the standard. After the data collection, all patterns were background

Table 2. Characteristics of the Thermoset Precursors

Name	Chemical Structure	Molar Mass (g/mol)
Diglycidyl ether of bisphenol-A (DGEBA)		344 n=0.03
4,4´-methylenebis-(3-chloro 2,6-diethylaniline) (MCDEA)		380

corrected and normalized with respect to thickness and, subsequently, were radially averaged, yielding 1D SAXS patterns of $I(q)$ vs q, q being the scattering vector ($q = 4\pi \sin \theta/\lambda$, and 2θ being the diffraction angle). The software package Fit2D [http://www0.esrf.fr/computing/scientific/FIT2D/] was used to perform background subtractions, spatially correct the diffraction patterns, and calculate integrations of scattered intensity. The setup of the apparatus enabled a resolvable range of $0.05\ \text{nm}^{-1} \leq q \leq 2\ \text{nm}^{-1}$. All peaks appearing in the 1D patterns were subsequently fitted with Lorentzian functions by using Origin, and in the case of the weak reflections, the Lorentz correction was also applied to the data.

Differential Scanning Calorimetry (DSC). Thermal analyses were performed by using a Mettler Toledo DSC-822 with nitrogen flux. Dynamic scans were performed at a heating rate of 10 °C/min. Reactivity of epoxidized copolymers was studied by performing dynamic scans on copolymer/MCDEA blends with a mass ratio similar to those used for ternary blends (which means a copolymer/MCDEA mass ratio of 1.2:1). Binary blends were prepared by solvent-casting in THF. The corresponding ternary blends were prepared by using an amino-hydrogen-to-epoxy stoichiometric ratio equal to 1 between DGEBA and MCDEA.

Results and Discussion

It should be noted that the following results refer to the bulk behavior of these systems because the cured blends have been prepared in a parallelepiped mould of 1.5-mm thickness.

Morphology of Cured Blends. The morphology of cured blends has been investigated by TM-AFM and TEM. The effect of epoxidation degree on the morphological behavior of neat star copolymers has been reported in a previous paper,[27] showing a transition from lamellar morphology for the SB copolymer to a hexagonal morphology for the epoxidized samples. AFM and TEM images for DGEBA/MCDEA cured blends containing 30 wt % copolymer are shown in Figure 1. It should be noted that cured blends containing both SB and SepB15 copolymers were opaque, thus indicating the presence of macroscopic phase separation. Alhough not shown, the SB copolymer macrophase-separates, forming a co-continuous structure, as revealed by optical microscopy. SepB15 copolymer also macrophase-separates, forming an inverted morphology, where epoxy-cured particles of around 3.5 μm are dispersed in a continuous copolymer matrix (Figure 1aI).

On the other hand, the fact that the cured blend morphology changes from co-continuous for SB to inverted phase morphology for a SepB15-modified system seems to be in contrast with the increase of miscibility between block copolymers and epoxy resin with epoxidation reaction. Nevertheless, as shown previously,[27] the epoxidation reaction leads to some secondary reactions that, in the case of low-epoxidation degrees, are recombination reactions that give an added increase of molecular weight of block copolymer, which may possibly be responsible or, at least, could influence the morphological behavior. It is well-known that the miscibility can be greatly influenced by the molecular weight.

For higher epoxidation degrees, the corresponding cured blends were transparent, thus suggesting the possibility of microphase separation and nanostructuring. As we have recently reported,[27] the epoxidation of PB block enhances the miscibility of the synthesized copolymers and the epoxy resin, thus leading to a nearly nanoordered structure for uncured blends, even for a high epoxy resin content. Typical AFM and TEM images clearly show nanostructuring through phase separation at nanoscale (Figure 1b−d). It should be noted that both AFM and TEM images have similar image size. Because of the OsO_4 staining, PB appears darker in the TEM images, while white and gray domains correspond to PS and the epoxy-rich phase, respectively. On the other hand, the PS domains appear darker and the PB domains appear white in the phase images of the AFM. It can be easily observed from Figure 1 that nanostructuring consists of PS cylinders arranged in the epoxy-rich phase. With respect to the location of PB and PepB units, a higher magnification of TEM images of these systems (Figure 1e−f) shows the presence of PB units in both the epoxy-rich phase and near to the PS cylinders.

The self-assembly for SepB61-modified system has been recently reported[28] as PS cylinders, with average radius of 11−13 nm, arranged in an epoxy-rich phase containing both epoxidized and nonepoxidized PB segments (denoted by the presence of dark domains in the epoxy-rich phase), which seems to indicate at least some partial miscibility of the PepB block with the cured-epoxy matrix as a consequence of the nonepoxidized segments of PepB block. Some differences can be observed with respect to the other epoxidation degrees. For the SepB40-modified system, Figure 1bI shows a broader size distribution for PS cylinders, with an average diameter of 20−35 nm, in comparison with higher epoxidation degrees. Moreover, the corresponding TEM image, Figure 1bII, clearly shows the formation of PS cylinders with different lengths and an average diameter of around 33 nm. For the highest epoxidation degree, however, a long-order hexagonal structure, similar to that shown for the SepB61-modified system, can be clearly observed. The domain size remains almost similar to that for the SepB61-modified system, both of them being slightly lower than that corresponding for the SepB40-modified system.

Hence, nanostructuring induced by self-assembling of the star block copolymers occurs at 40 mol % epoxidation degree and beyond. On the other hand, both AFM and TEM images show that, similarly to that observed for the SepB61-modified system, there is not a preferential orientation of the cylinders for the SepB40 and SepB76-modified systems, as can be seen, for example, in Figure 1bII and on the top of the left corner of

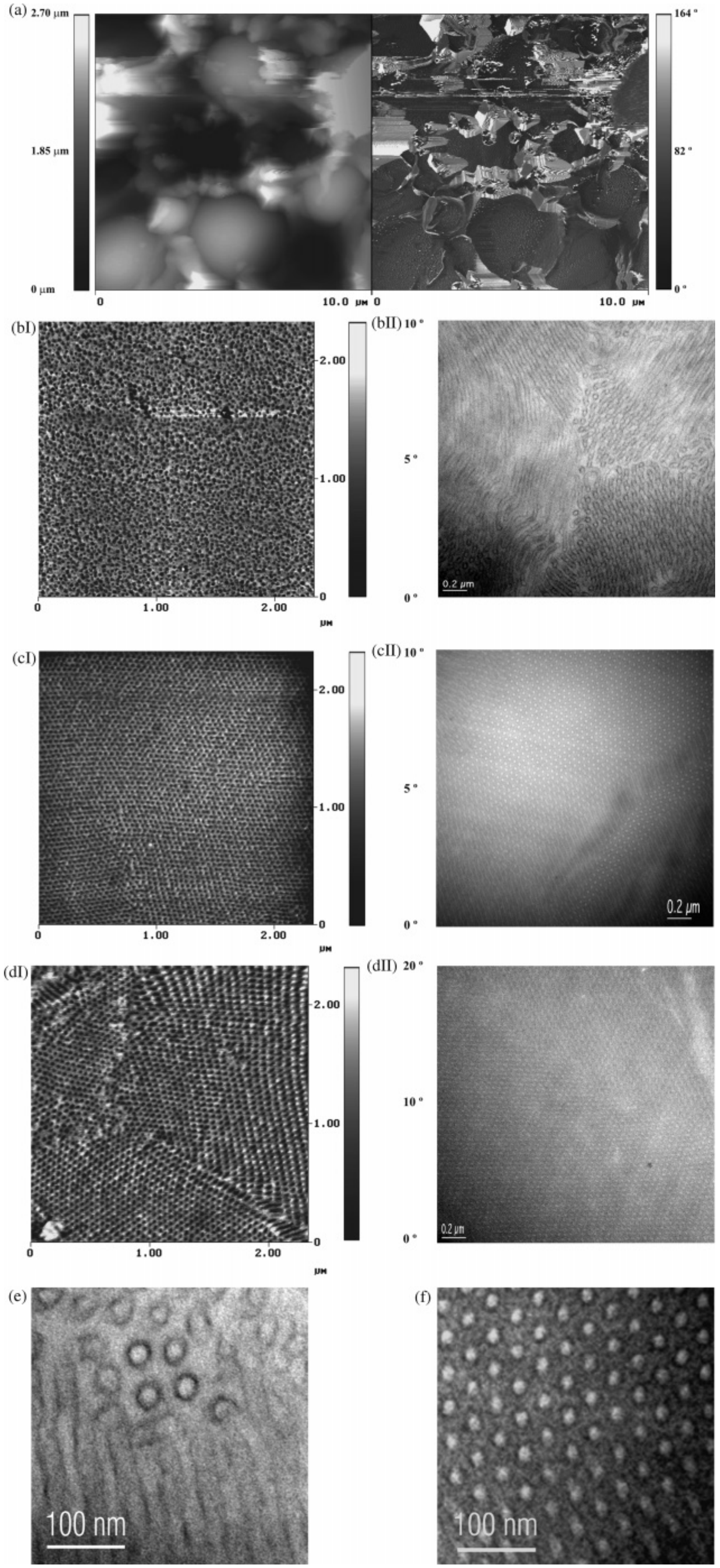


Figure 1. TM-AFM phase (I) and TEM (II) images for DGEBA/MCDEA blends containing 30 wt % of: (a) SepB15, (b) SepB40, (c) SepB61, and (d) SepB76 copolymers. (e and f) Figures show higher magnification of TEM images for SepB40- and SepB61-modified systems, respectively. For TEM observations, the samples have been stained with OsO_4 for 4 min. The left AFM image shown in (a) corresponds to the topographical image.

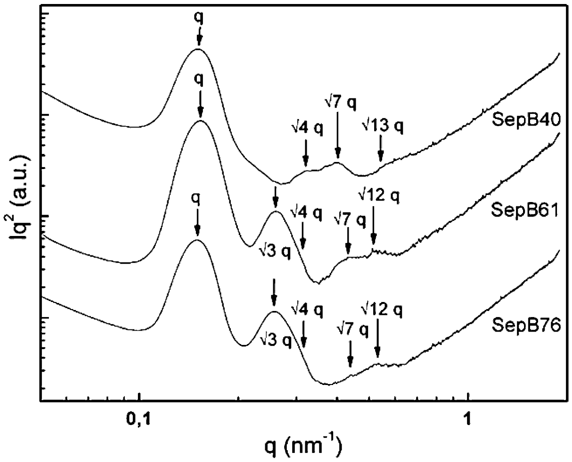


Figure 2. SAXS pattern for DGEBA/MCDEA blends containing 30 wt % SepB40, SepB61, and SepB76 block copolymers. The arrows indicate the different reflections.

Table 3. Long Spacing in Real Space for DGEBA/MCDEA Blends Containing 30 wt % SepB40, SepB61, and SepB76 Block Copolymers

	SepB40	SepB61	SepB76
d^*_{SAXS} (nm)[a]	41.9	40.9	42.1

[a] $d^* = 2\pi/q^*$, where q^* is the position of the main peak.

Figure 1dI, which is consistent with the method used for the preparation of these samples.

SAXS measurements performed at room temperature for nanostructured systems have confirmed that there is no preferential orientation of the PS nanodomains in the samples. SAXS 1D patterns are shown in Figure 2, where the different reflections for the hexagonally systems are indicated by arrows. As can be observed, blends with an epoxidation degree equal or higher than 40 mol % present a slightly broad first-order scattering peak, which was fitted with a Lorentz function to determine the main peak position, q^*. Table 3 shows the long spacing in real space for the main peak, obtained from the value of the scattering vector q^* corresponding to this peak. As can be seen, there are not strong differences in the long spacing between the different systems because the repeated distance between PS cylinders for all the blends is around 41−42 nm.

As far as the structure is concerned, the observed reflections for SepB61-modified system correspond to relative q spacings of: 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, and $\sqrt{12}$, which is consistent with what is expected for the hexagonally ordered structure observed by AFM and TEM and also determined through a 2D Fourier-transformed power spectrum from AFM images.[28] A similar behavior can be observed for the highest epoxidation degree. For the SepB40-modified system, however, the reflections corresponding to the basal plane of the cylinders (which corresponds to (110) spacings) disappear, and the relative q spacing of $\sqrt{12}$ appears slightly displaced. This behavior may be attributed to some loss of local ordering, probably associated to the broader size distribution of the PS cylinders that may lead to a more imperfect packing,[30] as well as with a slight morphological change due to the changes in the molecular mass of the epoxidized block copolymer.

Therefore, SAXS measurements confirm the formation of a hexagonally ordered structure for these systems as observed by TEM and AFM, revealing also a slightly different nanostructure for the SepB40-modified system.

Dynamics of Cured Blends. Taking into account the morphological behavior of cured blends, the characteristic relaxations for different cured blends have been analyzed. Figure 3 shows dynamic mechanical spectra for the cured neat DGEBA/MCDEA system and its blends containing 30 wt % SB and different epoxidized SB block copolymers in both low- and high-temperature ranges (Figure 3a and b, respectively). The neat DGEBA/MCDEA system exhibits two relaxation processes with increasing temperature. The first one, centered around −65 °C, corresponds to β relaxation mode, associated with the sum of localized motions of the glycerol groups and the diphenylpropane units in the network chains,[31,32] and the second one, around 162 °C, corresponding to the α relaxation mode, associated with glass transition temperature, T_g.

Spectra for the 30 wt % SB and SepB15-modified systems have been analyzed by comparison with those corresponding to the neat SB copolymer, PS homopolymer, and their corresponding cured blends containing 15 wt % modifiers (Figure 4). It should be noted that cured blends containing both SB and PS homopolymer were opaque, thus clearly indicating the presence of macroscopic phase separation. In the low-temperature range, Figure 3a, a main relaxation appears at around −85 °C or −70 °C for the 30 wt % SB and SepB15-modified systems, respectively. By taking into account that these values are similar to the T_g's measured by DSC[27] for PB and PepB block in neat SB and SepB15 copolymers, respectively, and on the other hand, that the shape of these relaxations are similar to PB main relaxation in neat SB (Figure 4), it is inferred that these relaxations can be attributed to the α relaxation mode of PepB block, which is overlapping with the β relaxation of the epoxy-rich phase. It should be mentioned that the small relaxation that appears at around −30 °C for the 30 wt % SB-modified system could be attributed to the PS−PB interphase because, on one hand, it does not appear for neat and modified PS systems, and on the other hand, it does not vary when SB content increases from 15 to 30 wt % and it appears for neat SB copolymer. For the 30 wt % SepB15-modified system, in addition to the relaxation corresponding to copolymer interphase, which appears at around 0 °C, a shoulder appears at around −110 °C, which is associated with less-restricted PB or PepB chains, probably due to the broad molecular weight distribution observed for neat copolymer.[27] On the other hand, the α relaxation mode for PS block appears around 90 °C for these systems, while the corresponding one to epoxy-rich phase could not be detected because the samples were broken prior to reaching this temperature, thus suggesting that the copolymers form the matrix in the blend. The corresponding spectrum for the 30 wt % SB-modified system without postcuring and obtained at lower forces (not shown here) has revealed a T_g for the epoxy-rich phase near to the cure temperature. Relaxations associated with glass transition temperatures for each block in SB appear to be practically unaffected by the epoxy network, thus confirming phase separation between SB and epoxy network. Similar behavior for epoxy resin/SB diblock copolymer cured blends using 4,4′-diaminodiphenylmethane (DDM) as a hardener has been reported by Guo et al.,[33] who observed that SB blended up to 10 wt % macrophase-separated, forming irregular shaped domains in a continuous epoxy matrix that changed to a co-continuous morphology when the SB content increases up to 30 wt %.

Similarly, the spectrum for a 30 wt % SepB15-modified system without postcuring and obtained in torsion mode using an Advanced Rheometrics expansion system (ARES) rheometer (not shown here) revealed similar values for the T_g for the PS block and a T_g for the epoxy-rich phase at around 125 °C. Thus, the inverted macroseparated morphology already observed by

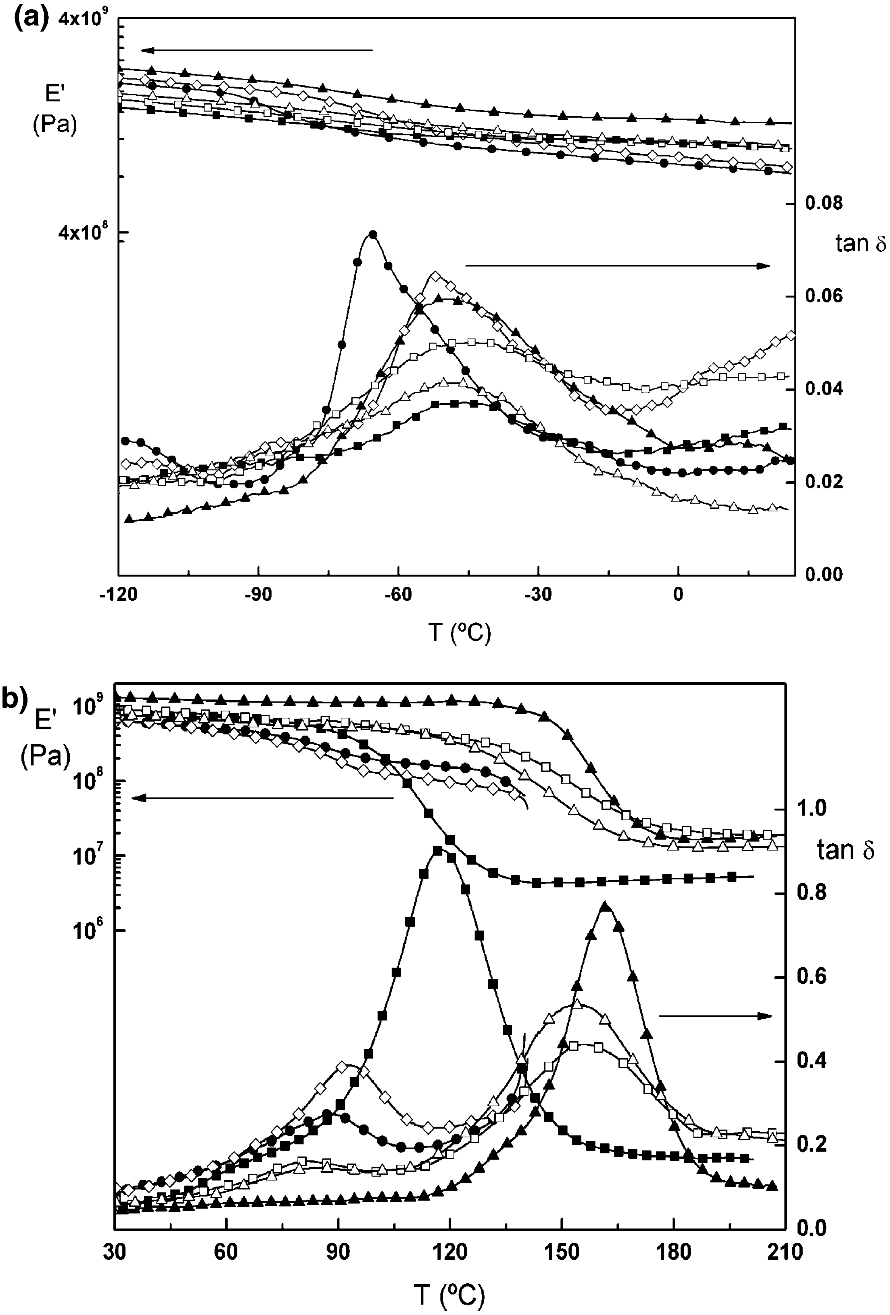


Figure 3. Dynamic mechanical spectra obtained at 1 Hz for neat DGEBA/MCDEA system (−▲−) and its blends containing 30 wt % of: (−●−) SB, (−◇−) SepB15, (−■−) SepB40, (−□−) SepB61, and (−△−) SepB76 copolymers: (a) low-temperature range and (b) high-temperature range.

morphological analysis is confirmed. Moreover, it seems that the increase of the viscosity induced by the addition of the copolymer leads to a decrease of the rate of cross-linking reaction, thus resulting in an incomplete curing reaction.

When the epoxidation degree increases up to 40, 61, or 76 mol %, only one process, corresponding to the β relaxation of the epoxy-rich phase, has been observed in the low-temperature range (Figure 3a). The corresponding T_g's for PepB blocks in neat copolymers appeared at around −50, −30, and −23 °C, respectively.[27] This fact suggests that PepB units are not separated from the epoxy matrix. Moreover, the T_g of PS appeared separated from the epoxy-rich phase, thus suggesting the self-assembling in cured blends, which is consistent with the morphological analysis. Nevertheless, strong differences can be observed between SepB40 and highly epoxidized copolymers in the high-temperature range. The spectrum for SepB40-modified system shows a broad α relaxation process for epoxy-rich phase centered at around 120 °C and slightly overlapped with the T_g for the PS block. The shift of α relaxation of the epoxy-rich phase to lower temperatures with respect to the neat system and, on the other hand, the higher height of tan δ curve for this system, could indicate a plasticization effect induced by the incorporation of the PepB block in the epoxy network, which could be attributed to miscibility or to some degree of reaction between SepB40 and MCDEA. Consequently, it could explain the different morphological behavior observed for this system in comparison with higher epoxidation degrees because both T_g's for the PS and epoxy-rich phases for these systems appear at around 80 and 155 °C, respectively.

It is worth noting that, after the α relaxation of the epoxy-rich phase, the systems modified with 30 wt % SepB40, SepB61, and SepB76 have an elastomer-like behavior, which means that

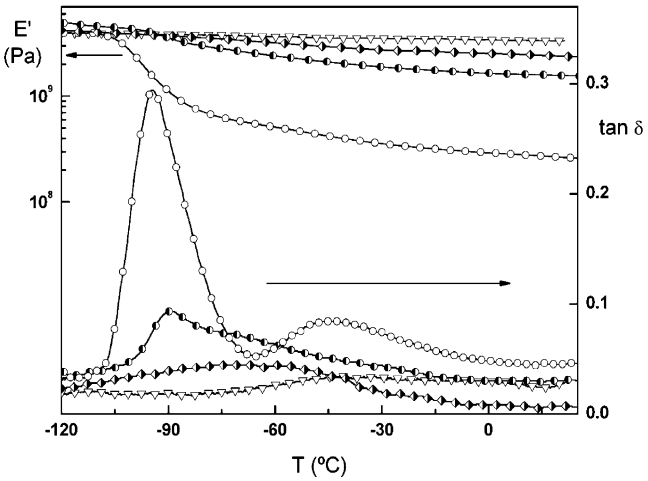


Figure 4. Dynamic mechanical spectra in low-temperature range obtained at 1 Hz for SB copolymer (−○−), PS homopolymer (−▽−), and epoxy blends containing 15 wt % SB copolymer (−◐−) and PS homopolymer (−diamond, right-filled−).

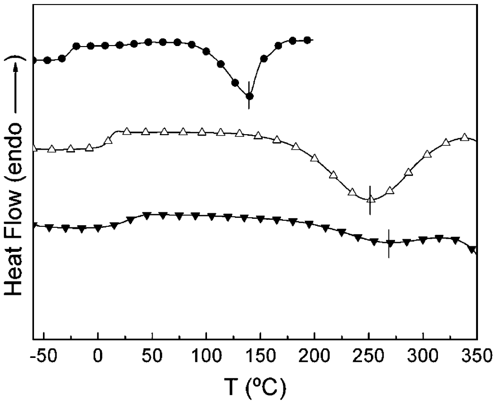


Figure 5. DSC dynamic scans for: neat DGEBA/MCDEA system (−△−), blend containing 30 wt % SepB40 block copolymer (−▼−), and SepB40/MCDEA blend prepared as described in Experimental Section (−●−). Normalized data: the curves have been normalized by taking into account only the epoxy equivalents.

these systems are thermosetting materials with an epoxy matrix. Additionally, the rubbery modulus values for SepB40-modified system are lower than those corresponding to systems modified with higher epoxidized copolymers, which is consistent with a lower cross-link density for this system. Thus it is inferred that higher epoxidation rates are needed to retain the stiffness at higher temperatures.

The key questions still persisting though are two: (i) if the presence of the PepB block in an epoxy matrix, observed by DMA and morphological analysis, is due to the reaction of PepB block with hardener through the epoxidized units, or only simply because of miscibility between the block copolymer and the epoxy resin, and (ii) if the different behavior between SepB40-modified system and the corresponding cured blends containing copolymers with higher epoxidation degrees is due to reactivity differences of the block copolymers with MCDEA.

Reactivity of SepB*x* in Epoxy/MCDEA Blends. DSC dynamic scans for neat DGEBA/MCDEA, the SepB40-modified system, and the SepB40/MCDEA blends are shown in Figure 5. For the SepB40-modified system, after mixing the components, the initial T_g appears to be quite higher than that corresponding to the neat DGEBA/MCDEA system. As described in the Experimental Section, MCDEA was added to the blend at 140 °C. By taking into account that, at these temperatures, SepB40 shows the maximum reaction rate with MCDEA and, on the other hand, the lower initial T_g for SepB40/MCDEA blend, this increase can be attributed mainly to reactions between the copolymer and MCDEA. Thus, the smaller exotherm shown at higher temperatures could be attributed to some amine consumption during the mixing step.

It should be mentioned that, after mixing, the corresponding analysis for copolymers with higher epoxidation degrees (not shown here) showed a lower T_g value than for the SepB40-modified system and a small exotherm starting around 140 °C, thus indicating that these copolymers are able to react with MCDEA, but at a comparative rate to that for epoxy resin. As far as the first key question above established, it seems that, for all the nanostructured systems, the presence of the PepB block in an epoxy matrix is due to the reaction of PepB block with hardener through the epoxidized units.

On the other hand, these results allow us to explain the strong difference on dynamic and morphological behavior between intermediate and highly epoxidized copolymers in the cured blends. For the SepB40-modified system, the SepB40 copolymer reacts during blend preparation with MCDEA, thus leading to a stoichiometric imbalance and, consequently, to a hindering in the polymerization reaction of the epoxy phase. These features are consistent with the lower T_g and rubbery modulus values for this system in comparison with those for SepB61- and SepB76-modified systems. For higher epoxidation degrees, however, the self-assembly process seems to be similar to those corresponding to epoxy blends mixed with linear copolymers with reactive blocks (e.g., GMA-containing blocks),[7,9] where the copolymers cure within the epoxy matrix at a comparative rate. Further work is currently underway in order to quantify chemical reactions between components and also the final properties of these blends.

Conclusions

In the present work, a systematic study of the effect of several epoxidation degrees of butadiene block in a commercial polystyrene−polybutadiene star block copolymer have been systematically investigated to control nano-ordering in thermosetting epoxy systems. For this purpose, DGEBA/MCDEA blends containing 30 wt % neat SB and several epoxidized SB star block copolymers have been synthesized.

At low epoxidation degrees, interactions with the epoxy matrix are not sufficiently favorable and macroscopic phase separation takes place, leading to a phase-inverted morphology where the block copolymer may become the matrix. For high epoxidation degrees, however, nanostructured thermosetting systems, being the epoxy-rich phase of the matrix of the blends, have been obtained. It has been proved that, in blends containing SepB61 and SepB76 star block copolymers, the copolymer self-assembles into a well-defined hexagonally ordered structure, where the cylinders are formed by PS arranged in an epoxy matrix containing both epoxidized and nonepoxidized butadiene units. Nevertheless, some domains of different structure are present on the SepB40-modified system. The SAXS experiments showed that there are not any strong differences in the long spacing between the different systems because the repeated distance between PS cylinders for all the blends is around 41−42 nm.

On the other hand, while macrophase separation is avoided for both intermediate and high epoxidation degrees, chemical reactions occur at different rates depending on the epoxidation degree. The reactive copolymers can react with amine at a comparative rate to epoxy resin, but this behavior depends on epoxidation degree. This behavior has been observed for SepB61 and SepB76 star block copolymers used in this study, obtaining long-range ordered thermosetting nanostructures. Contrary to what might have been expected, the SepB40 star copolymer reacts with the amine at a higher rate than it reacts with the epoxy resin in the SepB40/DGEBA/MCDEA blend, leading to a hindering in the epoxy polymerization reaction and, consequently, to a slightly less-ordered structure in comparison with higher epoxidation degrees on the block copolymer.

Thus, epoxidation of a commercial cheap SB star block copolymer beyond 40 mol % epoxidation degree is an effective way for the preparation of novel nanostructured materials based on thermosetting matrixes, with potentially advanced mechanical properties and retention of the optical transparency of the epoxy matrix.

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