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Nanostructured Thermoplastic Elastomers Based on SBS Triblock Copolymer Stiffening with Low Contents of Epoxy System. Morphological Behavior and Mechanical Properties[†]

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ABSTRACT: We report an approach for the design of nanostructured thermoplastic elastomeric materials consisting of poly(styrene-b-butadiene-b-styrene) and epoxy. This approach consists in the epoxidation of PB block and further mixing with low contents of the DGEBA:MCDEA system. Morphological behavior as well as thermal and mechanical properties have been investigated. The modification of epoxidized SBS with 10, 20, and 30 wt % epoxy system induces microphase separation at nanoscale from a poorly to well-ordered self-assembled morphology where the shape of these structures depends greatly on the mixture compositions, showing a transition from worm-like to lamellae. The generated nanostructures are accessible owing to the miscibility between the epoxidized PB block and the epoxy system that have been confirmed by an increment on the T_g (before and after curing) of this block in the mixture. The mixing produces a significant increase on strength and stiffness being more relevant in the system with 30 wt % epoxy and well-ordered lamellar morphology.
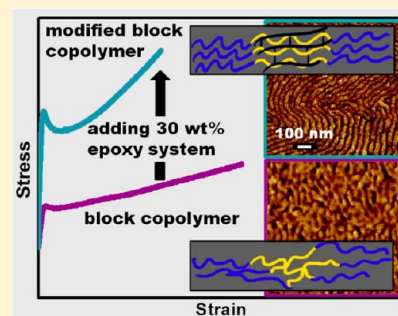
■ INTRODUCTION

Poly(styrene-b-butadiene-b-styrene) (SBS) triblock copolymers with 60−80 wt % soft phase fraction is one of the main commercial thermoplastic elastomers (TPE) due to their excellent mechanical properties as high tensile strength and elongation at break. SBS triblock copolymers present processability of a thermoplastic at high temperatures and elastic behavior at room temperature due to physical cross-links introduced by vitrification of PS domains. The mechanical behavior of SBS triblock copolymers has been widely reported, and their deformation mechanisms have been also discussed as a function of their self-assembled morphology and molecular architecture.[1−6] On the other hand, by mixing block copolymers with homopolymers, being the block copolymer amphiphilic with respect to the homopolymer, significant changes on morphology at nanometer scale can be achieved due to a selective confining of polymer miscible chains into one block of the copolymer. This approach allows to obtain a broader range of physical properties only by varying the ratio between components in the mixture, which is more desirable than the polymerization of a new material for each specific requirement.[7−14]

The synthesis of nanostructured thermosetting materials containing block copolymers as modifier has also been a great research interest in the past years due to the capability of block copolymers to act as templates for the synthesis of long-range order nanostructures embedded in thermosetting matrices.[15−21] The formation of nanostructures as a consequence of interactions between the thermosetting matrix and the modifier leads to an improvement on mechanical properties maintaining the transparency of the matrix.[22−26] Moreover, the block copolymers can be chemically modified in order to promote the compatibilization of

one block with the epoxy system. In previous works we have shown that poly(styrene-b-butadiene) (SB) block copolymers can be randomly epoxidized with hydrogen peroxide in the presence of a catalyst in a biphasic system.[27] This method of functionalization is a feasible approach to promote the compatibilization of PB block with the epoxy system and as result generate microphase-separated domains in the epoxy network after curing through the mechanism of reaction-induced microphase separation (RIMS) of PS block or through the self-assembly of epoxidized polybutadiene block before curing.[28−32]

In this sense, taking into account the demonstrated miscibility between epoxidized PB (PBep) block of the modified SBS copolymer with the uncured and cured epoxy system,[27−32] the aim of the present contribution is the design of nanoestructured TPE materials stiffened by the use of a thermosetting system as modifier at low contents, in order to evaluate the effect of this modifier on the phase behavior and mechanical properties of TPE. In contrast to our previous works where a thermosetting matrix was modified with low contents of TPE block copolymer (up to 50 wt % of epoxidized SBS),[31,32] here an epoxidized SBS triblock copolymer with a high content of polybutadiene block has been modified with an epoxy resin (up to 30 wt %) cured with an aromatic amine hardener. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to investigate the morphology behavior, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to evaluate thermal transitions, and tensile tests were performed to
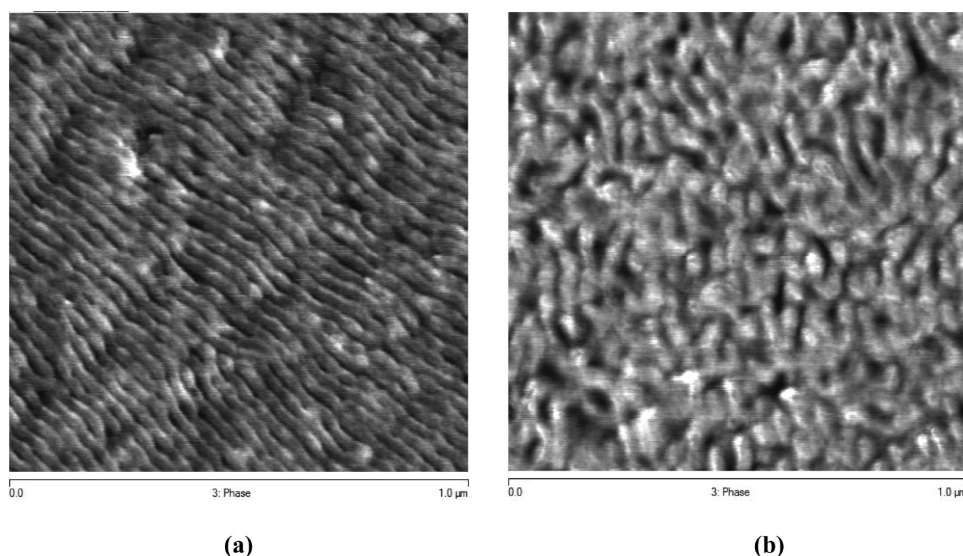
Figure 1. TM-AFM phase images of (a) SBS and (b) SBSep46 in bulk after annealing at 110 °C for 12 h. PB and PBep phase appears dark in AFM images.

study stress−strain properties of the novel nanostructured TPE materials. This study would provide a comprehensive explanation regarding the relationship between the chemical composition of TPE block copolymer/epoxy mixtures on the mechanical properties.

■ EXPERIMENTAL SECTION

Poly(styrene-*b*-butadiene-*b*-styrene) (Dynasol C540) linear triblock copolymer, with 60 wt % PB, was kindly supplied by Repsol-YPF. The weight-average molecular mass was 111 000 g/mol, and the glass transition temperatures (T_g) of PS and PB blocks were 82 and −84 °C, respectively. SBS triblock copolymer was epoxidized at 46 mol % with respect to PB double bonds, SBSep46. The epoxidation reaction of double bonds in SBS was carried out using hydrogen peroxide in the presence of an *in situ* prepared catalyst system in a water/dichloroethane biphasic medium. The details of the reaction are described elsewhere.[33] The T_g of epoxidized PB block, PBep, was −31 °C while the T_g of PS block remained unchanged in SBSep46. The increase of the glass transition temperature of PBep block was due to the introduction of epoxy rings in PB blocks which caused an increase of the chain rigidity. The polydispersity index of neat SBS and SBSep46 measured by GPC, using a universal calibration method with polystyrene standards, was 1.49 and 2.35, respectively. The increment on polydispersity index upon epoxidation was discussed in an earlier paper.[27] The epoxy monomer used, diglycidyl ether of bisphenol A (DGEBA), DER 332, was kindly supplied by Dow Chemical. It had an epoxy equivalent around 175 and an average number of hydroxyl groups per two epoxy groups $n = 0.03$. The hardener used was an aromatic diamine, 4,4′-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA), which was a gift from Lonza. The DGEBA/MCDEA stoichiometric ratio equal to 1 was maintained for all prepared systems.

The mixtures of SBSep46 modified with 10, 20, and 30 wt % epoxy system, named throughout the paper as 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy, respectively, were prepared in the following way: first, triblock copolymer, DGEBA resin, and MCDEA were dissolved in dichloroethane at a concentration of 5 wt %. The residual solvent was removed from the mixture at room temperature for 3 days under vacuum. Afterward, for the morphological and mechanical behavior in bulk of all nanostructured TPE materials, specimens of about 1 and 0.2 mm thickness were prepared by compression molding at 140 °C for 5 min. Finally, the resultant bulk specimens were cured at 140 °C for 3 days and postcured at 165 °C for 2 h under vacuum. The temperature of curing reaction for the DGEBA:MCDEA system was established in previous works,[37−42] and the time of reaction was increased due to the dilution effect of BC content.

The morphological behavior was investigated by atomic force microscopy and transmission electron microscopy. AFM images were obtained with a Nanoscope IIIa scanning probe microscope (Multimode, Digital Instruments). Tapping mode (TM) in air was employed using an integrated tip/cantilever (125 μm in length with ca. 300 kHz resonant frequency). Typical scan rates during recording were 0.7−1 line/s using a scan head with a maximum range of 16×16 μm^2. Height and phase images were simultaneously recorded during scanning. For the analysis of results, Nanoscope image processing software was used. In order to check the repeatability of mixtures morphology, different regions of the specimen were scanned. Similar images were obtained, thus demonstrating the reproducibility of the results. For TEM and AFM analyses in bulk, extremely thin sections and flat surfaces of the inner side of 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy systems were obtained by cutting with a diamond knife using a Leica EMFC6 cryo-ultramicrotome at −80 °C. For TEM analyses the samples were selectively stained with OsO$_4$ in order to enhance imaging contrast between the PB and PS/epoxy phases. A Tecnai G2 20 twin microscope, operating at an accelerating voltage of 200 keV in bright-field image mode, was used for TEM analyses.

Glass transition temperatures were determined by using a differential scanning calorimeter (Mettler Toledo DSC-822) under a nitrogen flow of 20 mL/min, working with 5−7 mg samples in aluminum pans. Dynamic scans were performed from −60 to 160 °C at a heating rate of 10 °C/min. The values of T_g were determined at the inflection point of the change in heat capacity. Dynamic mechanical analysis was carried out on cured mixtures with an EPLEXOR 100N (Gabo Instruments) in tensile mode. Scans were carried out at a frequency of 1 Hz and a heating rate of 2 °C/min. The samples used were parallelepipedic bars ($24 \times 3 \times 1$ mm^3). During the scans the samples were subjected to a static strain of 0.05% and a dynamic strain of 0.01%.

Tensile tests were performed in a MTS insight 10 equipment with a load cell of 250 N and provided with pneumatic grips and rubber-coated faces designed to prevent slipping during the test. The mechanical properties were determined according to the ASTM D882 Test Standard Specifications for Thin Plastic Sheeting.[34] This test method covers the determination of tensile properties of plastics in the form of thin sheeting, including film less than 1.0 mm in thickness. Constant crosshead speeds of 10 and 100 mm/min were used to determine the tensile modulus of elasticity and elongation at break, respectively. Specimens sizes were strips of uniform width of 5 mm and 0.2 mm in thickness obtained by compression molding, and a grip separation of 10 mm was used. A width−thickness ratio of at least eight shall be used. At least five specimens were tested for each set of samples being the average values reported.
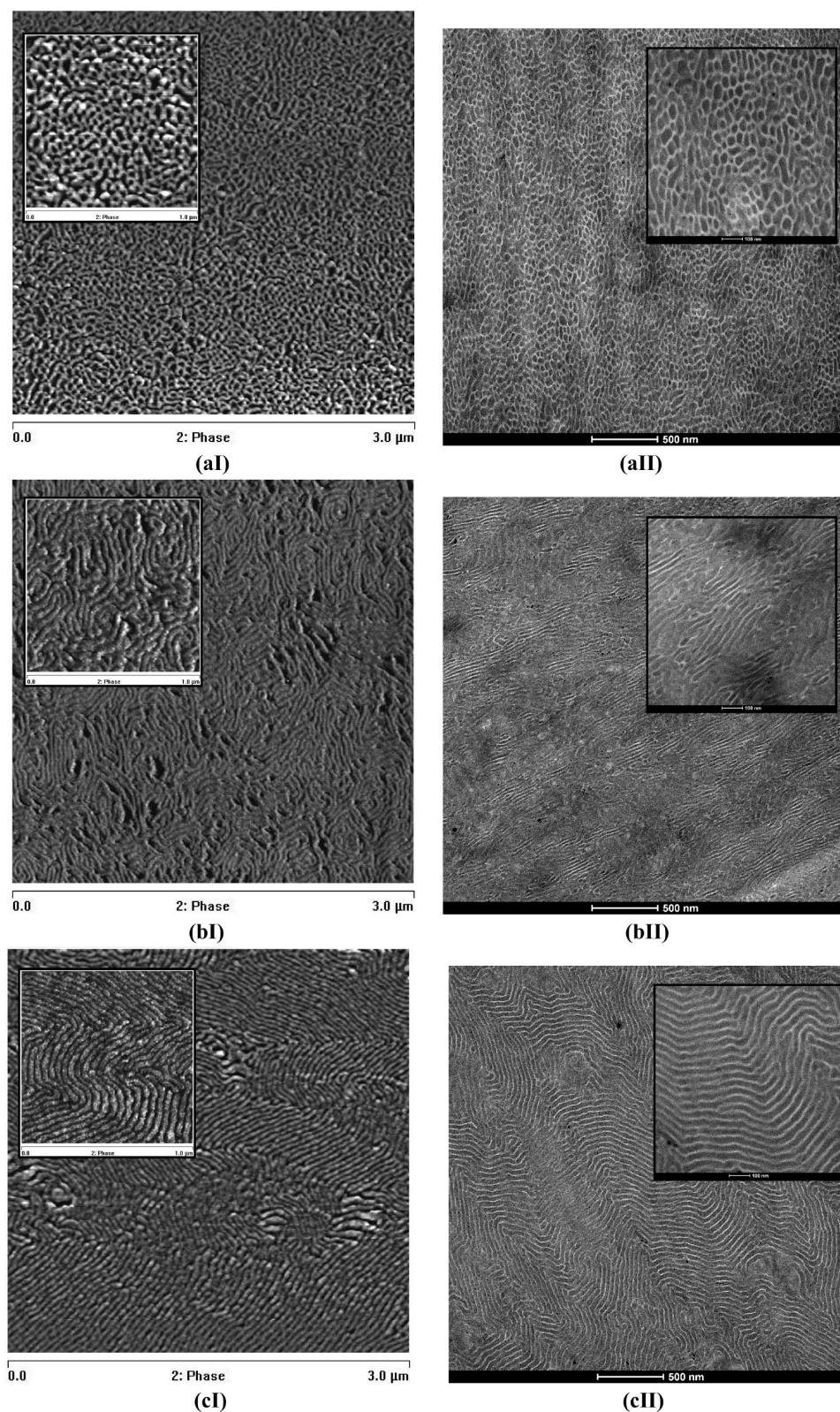
Figure 2. TM-AFM phase (I) and TEM (II) images of (a) 90SBSep46/10epoxy, (b) 80SBSep46/20epoxy, and (c) 70SBSep46/30epoxy systems in bulk after cured at 140 °C for 72 h and 165 °C for 2 h. PBep+epoxy phase appears dark in AFM images and black in TEM images.

■ RESULTS AND DISCUSSION

Characterization of Nanostructured Thermoplastic Elastomers in Bulk. The template generated in bulk by the self-assembled morphology of epoxidized SBS block copolymer was used to prepare nanostructured TPE modified with low

contents of epoxy system. In this sense, is important to evaluate the bulk morphology of neat block copolymers before mixing. Figure 1 shows the TM-AFM images of the self-assembled morphologies developed in bulk after annealing of neat SBS and SBSep46. As can be seen in Figure 1a, the neat SBS block
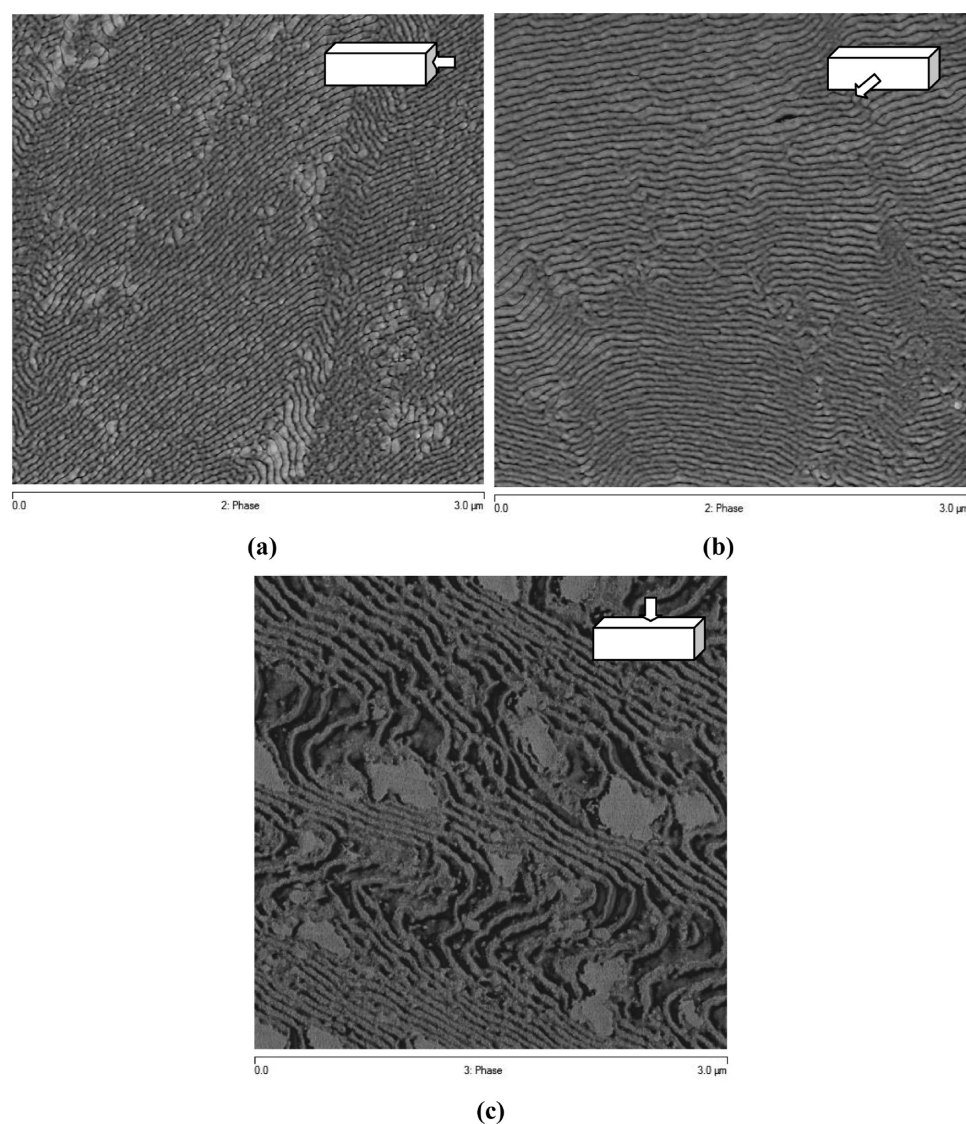
Figure 3. TM-AFM phase images in the inner of different directions in the 70SBSep46/30epoxy bulk system. The inset shows the corresponding scheme of analyzed sample directions. The PBep+epoxy phase appears dark in AFM images.

copolymer is able to self-assemble into a perfectly lamellar morphology with a specific value of periodicity distance around 33 nm and polystyrene lamellae of ∼20 nm thick. Moreover, after modification reaction, 46 mol % of epoxidation, the self-assembled morphology of SBS triblock copolymer changes significantly (Figure 1b); the epoxidized SBS block copolymer reveals a worm-like self-assembled morphology without long-range order, the specific value of periodicity distance around 40 nm, and polystyrene worms ∼30 nm thick. The differences in domain periodicity and self-assembled morphology between the SBS and SBSep46 block copolymers may relate to two factors: the well-known changes on polydispersity index and chemistry by introduction of oxirane groups into the butadiene chains after the epoxidation reaction.[27]

The increment on molecular weight and polydispersity index in the block copolymer by the epoxidation could hinder the molecular chains mobility delaying the formation of thermodynamic equilibrium and highly ordered structure. Besides, after epoxidation the thermodynamic degree of segregation χN between the two blocks could change owing to differences in solubility parameters by the introduction of oxirane groups.[27,35]

Other studies showed that an increase in polydispersity index has a significant effect on microphase-separated morphology of block copolymers; indeed, the domain periodicity generally increases as polydispersity index is increased in one block.[36−38] Lynd and Hillmyer[37,38] demonstrated that increasing the polydispersity index of majority domain can frustrate the chain packing into long-range order morphology.

Regarding the epoxidized SBS and epoxy mixtures, 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy, it should be pointed out that all bulk systems were transparent before and after curing reaction. These results suggest that cured mixtures were miscible or microphase-separated, as confirmed below by the TM-AFM and TEM analysis (Figure 2).

AFM phase and TEM images (Figure 2) reveal that the introduction of 10, 20, and 30 wt % DGEBA:MCDEA system into epoxidized SBS block copolymer induces microphase separation from a poorly ordered morphology in SBSep46 (Figure 1b) to well-ordered alternating lamellae in the 70SBSep46/30epoxy system (Figure 2c). It is plausible to propose that the epoxy network is interpenetrated in the PBep-block rich domains owing to the miscibility between these two components by the oxirane groups.[27−32]

Similar results were obtained by Tureau et al.;[14] they found by means of small-angle X-ray scattering (SAXS) and TEM that an ABC triblock copolymer can undergo an induced microphase separation from disordered to well-ordered structures using a copolymer/homopolymer mixture approach, and this phenomenon is related to the incorporation of the homopolymers chains into a selective block domains. Figure 2a reveals a bicontinuous morphology for the 90SBSep46/10epoxy system. The development of this morphology is due to the PBep-rich phase of epoxidized SBS block copolymer is swelled by the introdution of epoxy chains. The bicontinuous morphology has been reported as an intermediate morphology between the cylindrical and lamellar structure in block copolymers and mixtures.[36,39−44] Increasing the epoxy content up to 20 wt % (Figure 2b) led to changes in the morphology from bicontinuous to lamellar morphology with poor-range order (pseudolamellar); some parts of the lamellae are not completely formed, revealing the coexistence with a bicontinuous phase, and many disclination defects were observed (Figure 2b).[45−47] The morphology obtained in the 80SBSep46/20epoxy system could be assigned as a transition state between the bicontinuous structure developed in the 90SBSep46/10epoxy system and the achievement of a well-ordered lamellar morphology in the 70SBSep46/30epoxy system.

In previous works where a thermosetting matrix was modified with low contents of TPE block copolymer (up to 50 wt % of epoxidized SBS),[31,32] the mixtures revealed a transition from spherical to worm-like to cylinders of PS domains dispersed in a continuous phase of epoxy containing the PBep chains as the content of SBSep was increased. Thus, it is possible to expect that the mixture containing 70 wt % of SBSep46 and 30 wt % of epoxy system develops a lamellar structure. The main factors that govern the equilibrium phase morphologies in mixtures are the interaction parameter between each block and the solvent and the mixture composition.[48] Similar results were obtained by Hillmeyer and Lipic,[48−50] where a symmetric PEO−PEP block copolymer mixed with epoxy self-assembled into a lamellar array that can accommodate small amounts of epoxy (25 wt %). In conclusion, even though these developed nanostructures could be principally attributed to changes in the composition of the mixtures, other factors such as the homopolymer chemistry and chain length and its local segregation or reaction with a selective phase of block copolymer also may affect the final morphology of the mixture.[51−53]

In order to check the developed nanostructure in the 70SBSep46/30epoxy bulk system, the specimen was cut in different directions as shown in Figure 3, and thereafter AFM images in the transverse section of the inner of bulk specimen were obtained. As can be seen in Figure 3, similar nanostructures appeared in all directions.[45] In addition, Figure 3c shows different orientations of the microdomains, parallel (flat-on) and perpendicular (edge-on) lamellae domains to the cut surface.[44] The parallel lamellae is characterized by a continuous phase (Figure 3c). This fact confirms that the nanostructures developed in the 70SBSep46/30epoxy system are lamellae. We would like to emphasize that the lamellae microdomains orientation, parallel and perpendicular to the cut surface, has been reported by other authors in mixtures of block copolymers obtained by compression molding.[44] The coexistence of both perpendicular and parallel lamellae is because we have not employed a macroscopic orientation technique such as the flow alignment obtained by injection mold process; as a result, the lamellae microdomains are randomly oriented.[54,55]

The microphase separation behavior of nanostructured thermoplastic elastomers materials observed in TM-AFM and TEM images was confirmed by DSC (Table 1) and DMA analyses (Figure 4). DSC thermograms for all systems before

Table 1. Glass Transition Temperatures of Epoxidized PB-Rich Phase in the SBSep46 and Their Mixtures with 10, 20, and 30 wt % Epoxy before and after Curing Determined by DSC

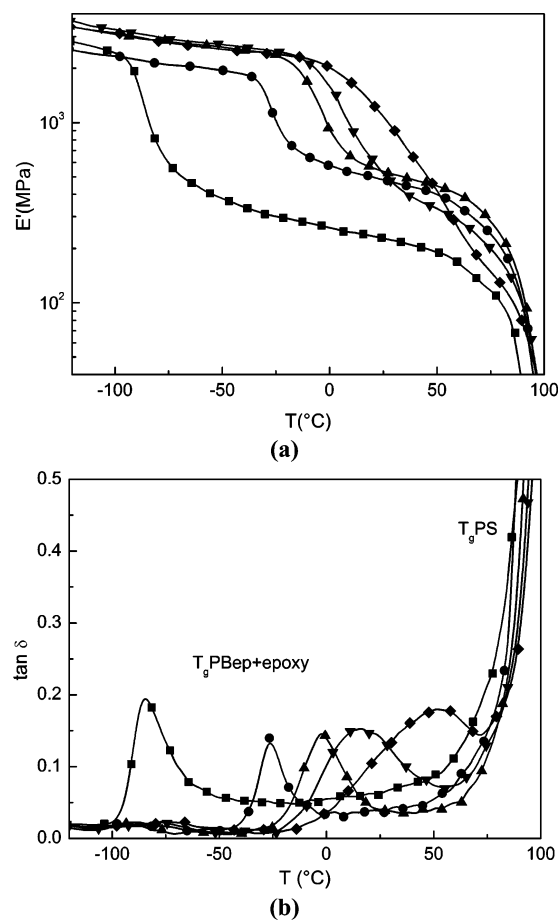| system	T_g matrix (°C)		ΔT_g matrix (°C)
	before curing	after curing	
SBSep46	−31		
90SBSep46/10epoxy	−23	−12	11
80SBSep46/20epoxy	−18	4	22
70SBSep46/30epoxy	−14	33	47

Figure 4. Storage modulus (a) and loss factor (b) of (■) neat SBS, (●) SBSep46, (▲) 90SBSep46/10epoxy, (▼) 80SBSep46/20epoxy, and (◆) 70SBSep46/30epoxy systems after curing.

curing reaction show the presence of two glass transition temperatures, giving a clear evidence of microphase separation between the components of the mixtures; one T_g is related with PS block which remains at a nearly constant temperature of around 80 °C for all mixtures, and another T_g is related to epoxidized PB-rich phase containing the epoxy system at lower temperatures. As can be noticed, the addition of 10, 20, and 30 wt % epoxy system drastically shifted the T_g of epoxidized PB phase from around −31 °C in neat SBSep46 to higher temperatures. Therefore, this fact confirms the strong influence of epoxy addition on the T_g related to epoxidized PB phase owing to the miscibility between the epoxy system and

SBSep46 before curing. After curing reaction the T_g of epoxidized PB phase is higher, as a result of an increment in the T_g of DGEBA:MCDEA due to the network formation, which could indicate that epoxy chains interacts with epoxidized group present in the PBep block. Previous studies about the possible cross-linking reaction of epoxidized PB block in these epoxy systems showed that the oxirane groups present in PB block are able to react with the thermosetting formulation. However, it was found that the reactivity of epoxidized PB units with the hardener was notably lower than that corresponding to the epoxy groups of DGEBA monomer.[29]

On the other hand, the relaxation process (δ-relaxation) and the phase miscibility of the mixtures were also investigated by means of the temperature dependence of loss factor, tan δ, and storage modulus, E'. Figure 4 presents the DMA profiles of SBS, SBSep46, 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy systems. These profiles show that the neat block copolymers, SBS and SBSep46, yield two characteristic relaxation processes: one at low temperatures related to the T_g of PB and epoxidized PB blocks in SBS and SBSep46 around −84 and −26 °C, respectively, and other at higher temperatures related to T_g of PS block around 82 °C for both block copolymers. It should be pointed out that the T_g at low temperatures is ascribed to the maximum of tan δ peak and the T_g at higher temperatures is ascribed to the initial point where the tan δ profile shows an increase. Similar results were obtained for 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy systems in DMA profiles, revealing two characteristic relaxation processes: one attributed to the T_g of epoxidized PB block phase that contains the epoxy network, around −2, 15, and 54 °C for 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy systems, respectively, and another at higher temperatures related to the T_g of PS block phase that remains almost unchanged with respect neat block copolymers, around 83 °C. The evolution of the T_g of epoxidized PB block rich phase with the epoxy content is in agreement with DSC results (Table 1). As can be seen, both the position and the width of the tan δ peaks are dependent on the epoxy content in the mixtures. As the content of epoxy systems increases, the T_g of epoxidized PB block phase is shifted toward higher temperatures due to a larger restriction of epoxidized PB molecular motion by the presence of a polymer network. The width of tan δ peaks is enlarged with the increase of epoxy content. The broadening of the δ relaxation could be attributed to the presence of different polymers networks into the epoxidized PB-rich phase. Taking all the results into consideration, we can conclude that the epoxy system and the epoxidized SBS block copolymer shows good miscibility. Regarding the variation of storage modulus behavior with the temperature, it should be point out that the storage modulus of block copolymer increases with the introduction of rigid epoxy chains. Besides, the storage modulus in the mixtures showed a thermoplastic-like behavior at higher temperatures, which means that the BC/epoxy mixtures could be processed at higher temperatures, a typical property of TPE materials.

The final mechanical properties of mixtures are usually conditioned by their microphase-separated morphology as well as the chemical constitution of the components of the mixtures. Stress−strain curves of SBS, SBSep46, 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy systems are presented in Figure 5. Tensile modulus, yield strength, and elongation at break are summarized in Table 2.

First, it is possible to emphasize that all curves shows characteristics of thermoplastic elastomeric materials (Figure 5). In spite of a reduction on strain at break values after epoxidation and mixing
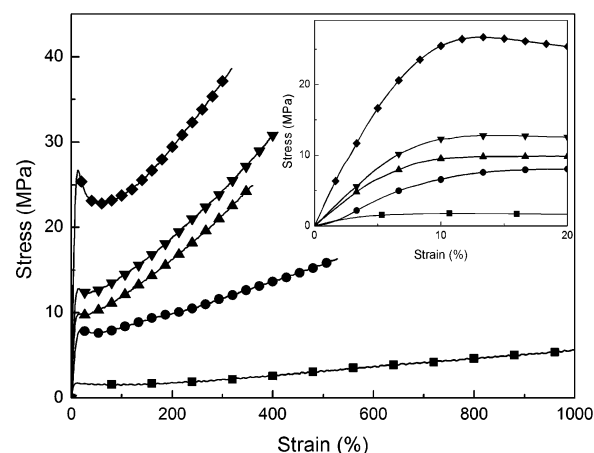

Figure 5. Stress−strain curves of (■) neat SBS, (●) SBSep46, (▲) 90SBSep46/10epoxy system, (▼) 80SBSep46/20epoxy, and (◆) 70SBSep46/30epoxy systems after curing. The inset shows a zoom at low deformations.

Table 2. Tensile Properties of Neat SBS, SBSep46, 90SBSep46/10epoxy, 80SBSep46/20epoxy, and 70SBSep46/30epoxy Systems

system	tensile modulus (MPa)	yield stress (MPa)	elongationat break (%)
SBS	38 ± 6	3.8 ± 0.3	2364 ± 259
SBSep46	109 ± 19	8.0 ± 0.4	509 ± 25
90SBSep46/10epoxy	141 ± 5	11.2 ± 0.7	325 ± 34
80SBSep46/20epoxy	159 ± 8	13.4 ± 0.6	372 ± 30
70SBSep46/30epoxy	372 ± 19	26.6 ± 1.5	307 ± 21

with epoxy system, these mixtures can be still considered as semiductile materials. This reduction on strain at break can be associated with a more restricted molecular mobility of soft segment. Tensile modulus of SBS triblock copolymer after epoxidation became significantly higher with the addition of epoxy system. This behavior is due to the stiffening effect by the presence of rigid epoxy chains in the soft elastomeric epoxidized PB phase. In fact, the 70SBSep46/30epoxy system has a higher increment on tensile modulus with respect to the neat SBSep46 than the 80SBSep46/20epoxy and 90SBSep46/10epoxy systems. A plausible explanation of the major increment in stiffness of the 70SBSep46/30epoxy system is the fact that, as can be seen from DMA results (Figure 4), this system is below the T_g of the PBep phase at the temperature of tensile test (room temperature), contrasting with the 80SBSep46/20epoxy and 90SBSep46/10epoxy systems. On the other hand, the PB epoxidation and mixing leads to a significant increase on yield stress. The yield stress of a material is ascribed to the resistance to plastic deformation. In this sense, the higher yield stress observed for the 70SBSep46/30epoxy system could be attributed to a larger amount of chemical linkages by some local cross-linking between the epoxidized PB block and the epoxy system, in contrast to the mixtures with lower contents of epoxy. The higher increment on tensile modulus and yield stress obtained in the mixture with 30 wt % epoxy could be due to a synergy effect by the increment of rigid chains and the development of a highly ordered morphology compared to the mixture with 20 wt % epoxy. Other studies demonstrated that both the shape and the range of order of self-assembled morphology could greatly affect the individual mechanical properties in TPE materials.[55−57] Furthermore, as can be noticed, the corresponding area under the stress−strain curves is higher for the 70SBSep46/30epoxy system.

A large area under stress−strain curves is ascribed to a much more absorbed energy which is a typical phenomenon of a tougher material.

Finally, it should be pointed out that the obtained results clearly show that the addition of low contents of epoxy system into the epoxidized SBS triblock copolymer is an effective way for the preparation of stiff nanostructured TPE materials. This approach could be used in many different applications, such as adhesives manufacturing, due to the excellent mechanical and optical properties that can be achieved.

■ CONCLUSIONS

The template generated by the self-assembly of SBS block copolymer has been successfully used for the design of a novel nanostructured TPE material containing rigid epoxy chains inside the soft PB phase by means of the epoxidation of double bonds of a SBS block copolymer and further mixing with low contents of an epoxy system (10, 20, and 30 wt %). Morphological and thermal analyses confirm the miscibility and selective confining of epoxy chains inside the PB-rich phase. The TPE/epoxy mixture approach induces microphase separation at nanoscale in SBSep46 from a poorly to well-ordered self-assembled morphology. The investigated mixtures reveal a transition from bicontinuous (10 wt % epoxy system) to a poor (20 wt % epoxy system) and well-ordered (30 wt % epoxy system) alternating lamellar morphology. Obtaining lamellar self-assembly in the mixture containing 70 wt % SBSep46 and 30 wt % epoxy system is expected taking into account our results in previous works.[31,32] Increasing the epoxy-amine content into the epoxidized PB-rich phase leads to a change in the width and the maximum temperature value of tan δ peak in the dynamic mechanical measurements. Tensile tests show a significant increase in stiffness and strength of SBS block copolymer through the mixing, retaining an interesting elongation at break value.

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Notes
The authors declare no competing financial interest.

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■ DEDICATION

[†]This work is dedicated to the memory of Professor Dr. Iñaki B. Mondragon (1954−2012), who founded the 'Materials + Technologies' Group in 1988 and who passed away after his contribution to this work. He was an inspiration for all of us.

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