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Synthesis and properties of epoxy resin modified with epoxy-terminated liquid polybutadiene

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Abstract

Epoxy resin networks have been modified with block copolymer of polybutadiene and bisphenol A diglycidyl ether (DGEBA)-based epoxy resin. Block copolymers prepared from isocyanate-terminated polybutadiene (NCOPBER) resulted in cured transparent epoxy networks with no discernible phase-separated morphology, as indicated by scanning electron microscopy. Epoxy resin modified with block copolymer derived from carboxyl-terminated polybutadiene (CPBER) presented an opaque aspect with dispersed rubber particle diameters in the range of 0.5–3μm. This value is substantially smaller than that found in epoxy matrix modified with hydroxyl-terminated polybutadiene. The different morphological characteristics observed in these modified systems were attributed to the different times to achieve the gelation (gel time) and also to the different structures of the block copolymers. The visual homogeneity of the NCOPBER block copolymer-modified network cannot be attributed to the presence of dissolved rubber, since the glass transition temperature of the epoxy matrix (determined from dynamic mechanical analysis) has not been substantially influenced by the presence of this block copolymer. The epoxy resin modified with the different block copolymers presented an improved impact resistance. The best mechanical performance in terms of flexural and tensile properties was achieved with the block copolymer derived from carboxyl-terminated polybutadiene, whereas a more flexible material has been obtained with NCOPBER block copolymer-modified network.

Keywords: Bisphenol A diglycidyl ether epoxy resin; Polybutadiene; Impact modifier

1. Introduction

Cured epoxy resins (ER) are extensively employed in several important applications such as structural adhesives, surface coatings, advanced composites for the aerospace and electronic industries, etc. because of their good engineering properties which include high stiffness and strength, creep resistance, chemical resistance and good adhesion to many substrates [1]. However, the major drawback of these resins is its brittleness in the cure state. It is well known that a small amount of reactive liquid rubber can greatly improve the fracture toughness of ERs by forming discrete rubbery particles chemically bonded to the matrix [2,3]. The use of low molecular weight rubber material is recommended to avoid an excessive increase of viscosity so that the processability of the system is not impaired [4]. The most popular rubbery modifying agent is carboxyl-terminated butadiene-acrylonitrile random copolymer (CTBN) because of its miscibility with the epoxy-hardener mixture during the initial polymerization period and also because the carboxyl functional groups in CTBN can react with the epoxide groups, thus achieving a high level of interfacial adhesion [5,6]. The enhancement in toughness is achieved because the elastomeric phase precipitates at some stage of the curing process into particles of very small size [7,8].

In order to ensure a complete reaction between the phases, the carboxyl-rubber is usually pre-reacted with an excess of the diepoxy resin. The resulting epoxide-rubber adduct participates in the polymerization with the hardener, leading to rubber covalently bonded to the matrix. This procedure has been performed with CTBN [9–11] and carboxyl-terminated acrylate rubber [12–15].

Epoxidized polybutadiene rubber has been also employed as a toughening agent for epoxy matrix [16–18]. The functionalization of hydroxyl-terminated

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liquid polybutadiene (HTPB) was obtained by reacting the unsaturations along the polymer backbone with an appropriate peroxy acid. The resulting epoxidized, hydroxyl-terminated polybutadiene (E-HTPB) contained internal oxirane groups, which increase the polarity of the rubber and consequently its compatibility with the ER. However, an effective adhesion between the phases is difficult to achieve because of the lower reactivity of the internal oxirane groups. An improvement of compatibility between ER and polybutadiene has been also achieved by the use of polybutadiene functionalized with carboxyl groups (CTPB) [19,20].

To increase the compatibility between HTPB rubber particles and epoxy matrix and to provide a better interfacial adhesion, it is important that both components are chemically joined resulting in a block copolymer. This can be achieved by first end-capping the polybutadiene with the epoxy molecules before the curing process, using a procedure similar to that one adopted in CTBN-modified epoxy resin. Such epoxy resin—polybutadiene block copolymers can be prepared from isocyanate-terminated polybutadiene (NCOTPB) or carboxyl-terminated polybutadiene (CTPB), whose synthetic schemes are represented in Figs. 1 and 2, respectively.

The aim of this work is to prepare both block copolymers constituted by polybutadiene and bisphenol A diglycidyl ether (DGEBA)-based epoxy resin and study the influence of the different ways to prepare them on the mechanical and morphological properties of corresponding epoxy-cured network systems.

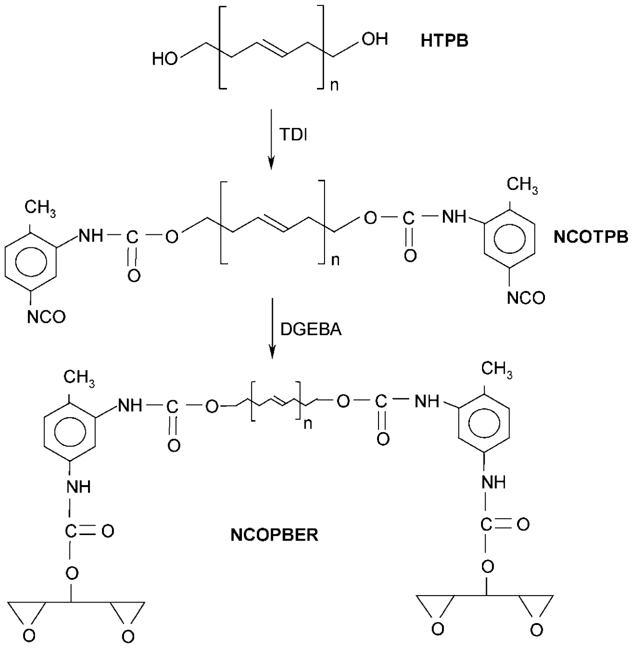

Fig. 1. Synthetic steps involved in the preparation of polybutadiene-epoxy resin block copolymer from isocyanate-terminated polybutadiene.

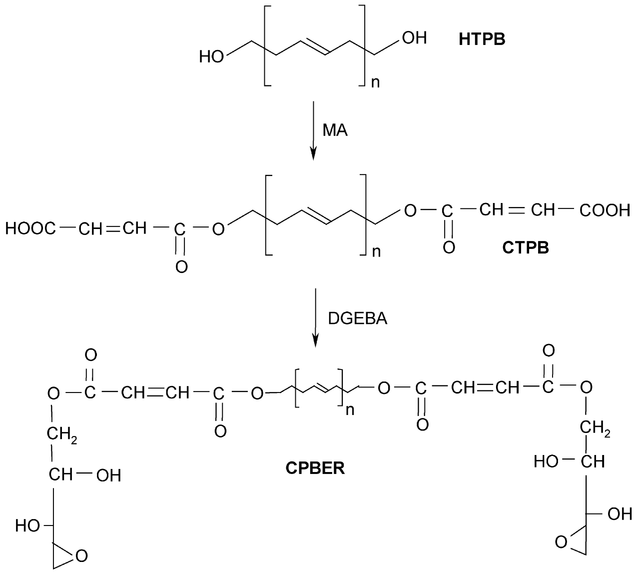

Fig. 2. Synthetic steps involved in the preparation of polybutadiene-epoxy resin block copolymer from carboxyl-terminated polybutadiene.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A (DGEBA)-based ER used in all experiments was EPON 828, with a number-average molecular weight ($\bar{M}_n$) of 380 and an epoxide equivalent of 192 g/equiv. as determined by acid titration. The cure agent was EPICURE 3140, a mixture of diethylenetriamine (DETA) and triethylenetetramine (TETA) with a number of amine groups corresponding to 378 g/equiv. Both the ER and the curing agent are produced by Shell Chemical Co. and was kindly supplied by Shell do Brasil S.A. HTPB (trade name: Liquiflex H, kindly supplied by Petroflex Ind. Com. S.A., Rio de Janeiro, Brazil) presents a $\bar{M}_n$ of 3000 and a hydroxyl number of 0.8 g/mequiv. Maleic anhydride (Vetec Ltda, Rio de Janeiro, Brazil) was distilled under vacuum before use. Triphenylphosphine kindly supplied by Merck do Brasil S.A. (São Paulo, Brazil) was used as received. All polymers were dried under vacuum for 24 h at room temperature before use.

2.2. Preparation of epoxide end-capped HTPB from isocyanate end-capped HTPB

The epoxide end-capped HTPB obtained by this procedure is denoted as NCOPBER (Fig. 1). This block copolymer was obtained by reacting the epoxy resin with different amount of isocyanate end-capped HTPB (NCOTPB) (5, 10 and 15 wt%) in the presence of dibutyl tin dilaurate as a catalyst, according to previous work [21].

2.3. Preparation of epoxide end-capped HTPB from carboxyl end-capped HTPB

The epoxide end-capped HTPB obtained from carboxyl end-capped HTPB (CTPB) is denoted as CPBER. The synthesis of CTPB was performed by reacting HTPB with maleic anhydride in a stoichiometric epoxy/anhydride molar ratio, as illustrated in Fig. 2. The reaction was performed in bulk at 80 °C for 24 h with magnetic stirring, under nitrogen atmosphere. The carboxyl content of CTPB was determined by titration with a methanolic solution of 0.10N NaOH using phenolphthalein as an indicator. The block copolymers were obtained by reacting the epoxy resin with different amount of CTPB (5, 10 and 15 wt%) and 0.2 wt% of triphenylphosphine. The reagents were added into a three-necked reaction flask blanketed with nitrogen. The flask was placed in an oil bath at 80 °C and allowed to react under stirring conditions for 24 h.

2.4. Curing procedure

The ER was modified with different amount of HTPB, NCOPBER or CPBER. All network polymers were prepared from mixtures of the ER and the hardener, EPICURE 3140 (see Table 1 for the formulations). ER/HTPB samples were prepared as follows: a proper amount of EPON 828 was first degassed for 60 min in a vacuum oven at 80 °C. The rubber (HTPB) was also degassed separately under the same conditions. Both components were mixed and the curing agent was added. The mixtures were gently stirred for about 5 min to ensure proper dispersion of the hardener, degassed for 5 min and poured into appropriated molds for mechanical testing. The cure was performed at 100 °C for 120 min. This cure condition was chosen from DSC studies performed in the static mode at 100 °C, which revealed that almost all curing processes happened before 60 min.

The network polymers prepared from epoxy-polybutadiene block copolymers were obtained by mixing NCOPBER or CPBER previously synthesized (containing pre-established proportion of epoxy-rubber) with the EPICURE 3140. The NCOPBER or CPBER samples were first degassed for 60 min in a vacuum oven at 80 °C. Then, the hardener was added and gently stirred for about 5 min. The resulting compositions were degassed for 5 min at 80 °C and poured into appropriated molds. The cure was performed at 100 °C for 120 min.

Table 1
Formulations and curing parameters of pure ER and those rubber-modified epoxy systems

ER (g)	Epicure (g)	HTPB (g)	NCOPBER[a] (g)	CPBER[b] (g)	ΔH^c (J/g)	Gel time (s)
100	25.4	0	0	0	290	225
95	24.1	5	0	0	280	225
90	22.8	10	0	0	280	225
95	24.1	0	5	0	285	165
90	22.8	0	10	0	285	165
95	21.7	0	0	5	280	190
90	20.6	0	0	10	280	190

[a] NCOPBER is the block copolymer obtained by end-capping the isocyanate-modified HTPB with the ER.

[b] CPBER is the block copolymer obtained by end-capping the carboxyl-modified HTPB with the ER.

[c] ΔH obtained from DSC measurements taken in the dynamic mode.

2.5. Characterization

Fourier transform infrared (FTIR) analysis was performed on a Perkin–Elmer 1720 spectrometer, at a 2 cm^{-1} resolution averaged over 20 scans.

Size exclusion chromatography was performed in a Water 600 liquid chromatograph equipped with two detectors (refractive index and ultraviolet) and three ultrastyragel columns with 500, 100 and 50 Å porosity. The molecular weight was determined from calibration curve using polystyrene standards and using the Millenium 32 program.

Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer DSC-7 equipment. The cure conditions were determined in a static mode at 100 °C and in dynamic mode at 10 °C/min under nitrogen. The static mode has been employed to verify the necessary time to complete the curing process and the dynamic mode was employed to calculate the enthalpy related to the curing process.

The gel point was determined according to ASTM 2471, by putting about 100 mg of the sample in several tubes, which were placed into an oil bath at 100 °C. The tubes were withdrawn from the bath at different times and chilled in an ice bath to quench the reaction. The polymeric material was dissolved with tetrahydrofuran (THF). The gelation point was determined from the presence of insoluble fraction.

The dynamical-mechanical measurements were made using a dynamical-mechanical analyzer DMA (TA INSTRUMENTS MODEL 2980). The measurements were carried out at the heating rate of 5 °C/min from −130 to 200 °C at fixed frequency of 3 Hz. The samples were rectangular bars 2.0 mm thick.

Scanning electron micrograph (SEM) was performed using a JEOL JSM-5610LV SEM with an electron voltage of 15 kV and secondary electron detector. The samples were handling fractured and the surface was first treated with chloroform to extract the rubber phase, then dried under vacuum and coated with a thin layer of gold before analyzing. The size and size distribution of the dispersed particle were determined by means of semiautomatic image analysis. The SEM micrograph of the fractured sample was first scanned and converted into digitized image, which was analyzed using an ‘AnalySIS 3.0’ program to obtain the average diameter values of the dispersed particles, d_n, and the particle size distribution.

2.6. Mechanical testing

Flexural tests were performed using an Instron 4204 testing machine fitted with a three-point bending fixture at a crosshead speed of 1 mm/min, according to ASTM D-790. The dimensions of the specimens were 75 × 25 × 2 mm and the span-to-thickness ratio was set at $L/D = 32$ to 1 in all cases. The values were taken from an average of at least five specimens.

The tensile tests were also performed in an Instron 4204 testing machine at a crosshead speed of 1 mm/min, according to ASTM D-638. The values were taken from an average of at least five specimens.

The impact strength of the notched specimens was determined by using a Charpy Monsanto Tensiometer, using rectangular specimens of 50 × 10 × 5 mm, according to ASTM D-256. The tests were carried out at room temperature and the values were taken from an average of at least ten specimens.

3. Results and discussion

3.1. Characterization of end-capped HTPB

The epoxide end-capped HTPB has been obtained by two different procedures: (a) coupling reaction of isocyanate end-capped HTPB (NCOTPB) with epoxy resin, resulting in NCOPBER (Fig. 1) or (b) coupling reaction of carboxyl end-capped HTPB (CTPB) with epoxy resin, resulting in CPBER (Fig. 2).

The synthesis and characterization of NCOPBER has been well discussed in previous work [21]. All isocyanate groups in the NCOTPB sample have been reacted with the hydroxyl groups of the ER, as indicated by the disappearance of NCO groups observed by FTIR analysis and NCO titration, which means that all functionalized polybutadiene were chemically bonded to the epoxy matrix. The epoxy equivalent weight of the sample containing 10 wt% of the NCOPBER block copolymer and 90 wt% of RE was similar to the neat epoxy resin (173 g/equiv.) because the NCO groups react preferentially with the hydroxyl groups (see Fig. 1).

The functionalization of HTPB with carboxyl groups (CTPB) is illustrated in Fig. 2. The amount of COOH group in the CTPB sample was determined by titration and corresponded to 0.5 mmol/g. This value is lower than the initial concentration of maleic anhydride employed in the reaction (0.8 mmol/g) and may be due to the sublimation of substantial amount of the anhydride during the reaction at 80 °C, confirmed by the presence of white needles in the upper part of the wall of the reaction flask.

Before curing, a large excess of epoxy resin was pre-reacted at 80 °C with CTPB in the presence of triphenylphosphine as a catalyst for 24 h. The modified samples containing the CPBER block copolymer were liquid and no gelling was observed after pre-reaction. This sample containing 10 wt% of the CPBER block copolymer and 90 wt% of RE presented an epoxy equivalent weight of 155 g/equiv., which is somewhat lower than the neat epoxy resin because some amount of the epoxy groups are consumed by the reaction with the carboxyl groups (see Fig. 2).

Fig. 3 presents the FTIR spectra of HTPB, the corresponding carboxyl-functionalized HTPB (CTPB) and the CPBER. An absorption at 1730 cm^{-1}, characteristic of carbonyl group of ester is observed in the spectrum of CTPB (peak a), indicating the incorporation of maleic anhydride into the HTPB chain. The spectrum of the CPBER sample is similar to that of the neat epoxy resin (not shown here) because of the high amount of this component in the system (90 wt%).

The block copolymers prepared by different methods (NCOPBER and CPBER) were analyzed by size exclusion chromatography (SEC). The chromatograms of these samples are presented in Fig. 4, together with those corresponding to the neat epoxy resin and HTPB. Both NCOPBER and CPBER samples display three peaks related to the fractions of the epoxy resin with different molecular weight (250, 400 and 720). Besides these peaks, the block copolymers display also another broad peak at similar elution volume related to the HTPB. This broad peak corresponds to the block copolymer because it can be detected by the ultraviolet detector, whereas the non-modified HTPB cannot be observed with this detector. The corresponding average-number molecular weight of this fraction was found to be around 2900 in both cases. This value is similar to the HTPB sample because the epoxy resin

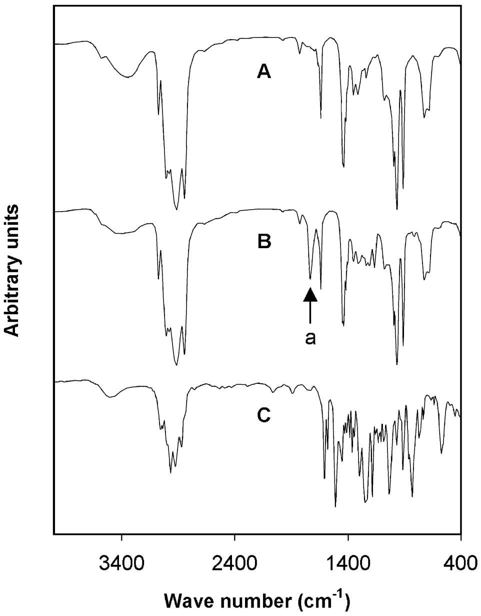

Fig. 3. FTIR spectra of (A) HTPB, (B) the corresponding carboxyl-functionalized HTPB (CTPB) and (C) the epoxy resin containing 10% of CPBER block copolymer.

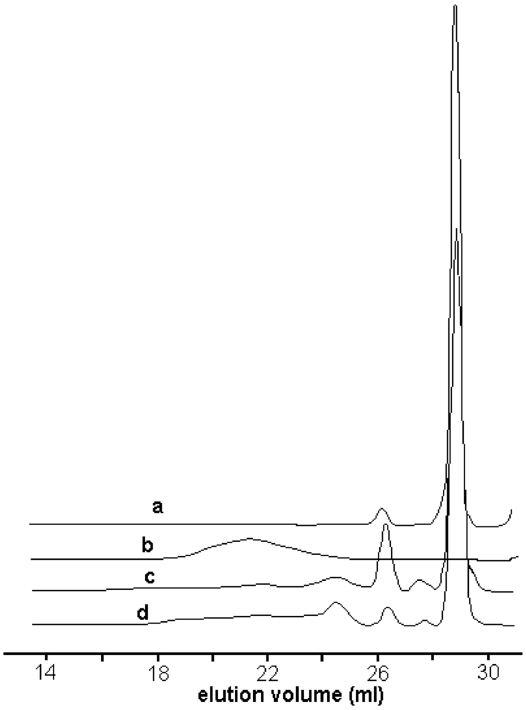

Fig. 4. SEC chromatograms of (a) epoxy resin; (b) HTPB; and the epoxy resin containing 10% of (c) CTPBER and (d) NCOPBER block copolymers.

chain that was incorporated to the functionalized HTPB has a low molecular weight.

These samples, containing different amount of the rubber component, were then cured with EPICURE 3140 at 100 °C for 2 h. The cured samples (about 1 g) were milled and treated with hot toluene to extract the rubber component that was not chemically bonded to the epoxy matrix. The CPBER sample presented an amount of soluble, non-reacted rubber corresponding to 10–15% of all rubber components in the mixture, indicating that almost all carboxyl-terminated rubber were chemically bonded to the epoxy matrix. NCOPBER sample did not present any extractable material indicating that all rubber components were well bonded to the matrix. It is important to emphasize that similar procedure carried out with epoxy resin containing non-functionalized HTPB resulted in a complete extraction of the rubber phase.

3.2. Evaluation of the cure parameters

The effect of the different epoxide end-capped HTPB on the cure parameters of the epoxy matrix is compared to that of non-modified HTPB in Table 1. The ΔH values related to the cure process were determined from the area of the exotherm peak obtained from DSC analysis, taken in the dynamic mode. This peak appeared during the first heating run but was completely absent during the second heating cycle. The presence of HTPB or the different block copolymers (NCOPBER or CPBER) did not affect significantly the ΔH values, indicating no influence on the crosslink degree of the epoxy matrix.

The necessary time to produce the minimum amount of insoluble material (gel time) was the same when pure ER or HTPB-modified ER was submitted to the reaction with the hardener. However, when epoxide end-capped HTPB was mixed with ER, a substantial decrease of gel time was observed, indicating that the systems containing the block copolymers crosslink faster than those consisted of pure ER or HTPB-modified ER. These results are quite different from those reported in literature for epoxy systems modified with CTBN [8] or carboxyl-terminated acrylate rubber [11]. The lowest gel time found in NCOPBER system may be attributed to the presence of urethane groups in the block copolymer, which may also participate in the curing process, accelerating the formation of the insoluble material.

The presence of CPBER block copolymer also decreased the gel time of the epoxy matrix but the difference was not as great as in the case of NCOPBER. It is believed that even after a long pre-reaction time of CTPB with an excess of ER, a small amount of free carboxyl groups in the rubber phase (which was not detected by titration) may be still present, which may also influence the curing process.

3.3. Mechanical properties

The impact strength, flexural and tensile properties of the cured ER samples containing different amount of the rubber agent are summarized in Table 2. Except that containing 15 wt% of NCOPBER, all other modified epoxy networks exhibit higher impact resistance than non-modified ER. The best performance was normally achieved with 10 phr of rubber. Above this optimum rubber content, a fall in the impact strength was observed. Similar behavior has been also reported in other rubber-modified epoxy systems and attributed to the agglomeration of rubber particles with the increase of the rubber concentration [15,18]. The presence of agglomerates acts as defects and initiates catastrophic failure.

Concerning the different epoxy-rubber systems, the addition of CPBER block copolymer containing around 10–15% of rubber resulted in the best impact resistance. The flexural properties were not affected by the addition of 5–10% of rubber in the form of CPBER block copolymer, when compared to the net epoxy network. Also, the best tensile strength has been achieved with this system. Epoxy matrix modified with NCOPBER also displayed very good impact strength when the amount of rubber was in the range of 5–10%, but the flexural strength and modulus decreased when compared to pure epoxy network. The data presented in Table 2 indicates that the way to prepare the epoxy-polybutadiene block copolymer affects the mechanical properties to a higher extent than impact behavior. The differences in mechanical behavior can be associated to morphological characteristics.

Table 2
Mechanical properties of rubber-modified epoxy networks

ER (%)	HTPB (%)	NCOPBER[a] (%)	CPBER[b] (%)	Impact strength (J/m^2)	Flexural yield stress (MPa)	Flexural modulus (MPa)	Tensile yield stress (MPa)
100	0	0	0	9.7 ± 0.4	83.8 ± 0.3	2536	54.3 ± 5.4
95	5	0	0	11.4 ± 0.4	72.0 ± 0.1	2385	50.2 ± 4.2
90	10	0	0	14.2 ± 0.4	62.2 ± 0.1	1912	50.4 ± 2.3
85	15	0	0	11.2 ± 0.4	60.0 ± 0.2	1860	46.0 ± 5.0
95	0	5	0	13.6 ± 0.3	67.0 ± 0.2	1753	70.0 ± 7.0
90	0	10	0	15.3 ± 0.4	70.0 ± 0.1	1776	52.6 ± 1.5
85	0	15	0	9.0 ± 0.9	62.3 ± 0.2	1523	45 ± 2.3
95	0	0	5	11.5 ± 0.3	92.0 ± 0.2	2350	90.4 ± 1.7
90	0	0	10	16.1 ± 0.4	82.0 ± 0.1	2300	84.1 ± 0.7
85	0	0	15	13.7 ± 0.3	66.0 ± 0.2	2166	63.5 ± 3.0

[a] NCOPBER is the block copolymer obtained by end-capping the isocyanate-modified HTPB with the ER.
[b] CPBER is the block copolymer obtained by end-capping the carboxyl-modified HTPB with the ER.

3.4. Morphology

The impact behavior of the toughened networks can be explained by considering both toughening and flexibilizing effects. The flexibilizing effect is caused by the presence of dissolved rubber inside the epoxy matrix, whereas the toughening process is related to the cavitation in rubber particles dispersed inside the epoxy matrix. According to Bucknall and Smith's theory, the rubber particles initiate the formation of crazes and control their growth [22,23].

In order to correlate the mechanical properties of the modified epoxy resin with the morphology, the fracture surface of rubber-modified epoxy networks was analyzed by SEM. The SEM micrographys of the toughened epoxy networks containing 10 wt% of HTPB, CPBER and NCOPBER are shown in Fig. 5. The micrographs of ER modified with HTPB shows distinct separated particles of rubber, indicating a heterogeneous system (Fig. 5(a)). This heterogeneous morphology resulted in opaque samples. The holes observed in the micrograph are related to the rubber particles that were withdrawn from the surface after the treatment with chloroform, indicating no chemical bond between the blend components.

Epoxy matrix modified with CPBER block copolymer is also visually opaque and presents a two-phase morphology in SEM micrograph (Fig. 5(b)). However, the size of the domains is considerably smaller than that observed for epoxy-HTPB system. In addition, one can observe the presence of several rubber particles that were not extracted with chloroform, indicating strong interfacial adhesion. This phenomenon is better observed in micrograph taken at higher magnification (Fig. 5(b)). This morphological situation is believed to be responsible for the highest impact performance.

Surprisingly, the epoxy matrix network modified with NCOPBER is visually transparent and homogeneous, indicating a single-phase system. The SEM micrograph of the fractured surface is homogeneous even after the treatment with chloroform, demonstrating no discernible phase separation and a complete adhesion between the blend components (see Fig. 5(c)). This characteristic has been also observed at a magnification as high as 10,000 (Fig. 5(c)). This result may be related to either total dissolution of the rubber inside the epoxy matrix or absence of particles above a critical size (≈0.15 μm). This morphology also results in good impact behavior.

The difference in particle size distribution for rubber particles greater than 0.1 μm in epoxy networks modified with HTPB or CPBER block copolymer were calculated from SEM micrographs, using at least a total of 100 rubber particles for each toughened system. The results are shown in Fig. 6. It is observed that epoxy resin modified with HTPB displays a large particle size distribution, with particle size diameters in the range of 0.1–75 μm, most of them situated in the range of 11–32 μm (Fig. 6(A)). In the case of epoxy resin modified with the CPBER block copolymer, the rubber particle size distribution is more uniform, with particle size diameters in the range between 0.5 and 3 μm (Fig. 6(B)). This range is similar to those found by Chen et al. in epoxy systems modified with epoxide end-capped CTBN [11].

The difference in morphology observed in both epoxy systems modified with epoxy end-capped HTPB (NCOPBER or CPBER block copolymers) may be attributed to the different gelation time in both systems. The system modified with NCOPBER presents fast gelation and more of the rubber can be trapped into the matrix. The cure process of the epoxy matrix takes place before the coalescence between the rubber particles. Consequently, the rubber domains cannot be observable by SEM. In addition, the structure of the block copolymer containing four epoxy units per chain may also turn difficult the coalescence process. In the case of CPBER-modified epoxy networks, the gel time is a little higher and the block structure is less hindered, increasing the chance of coalescence.

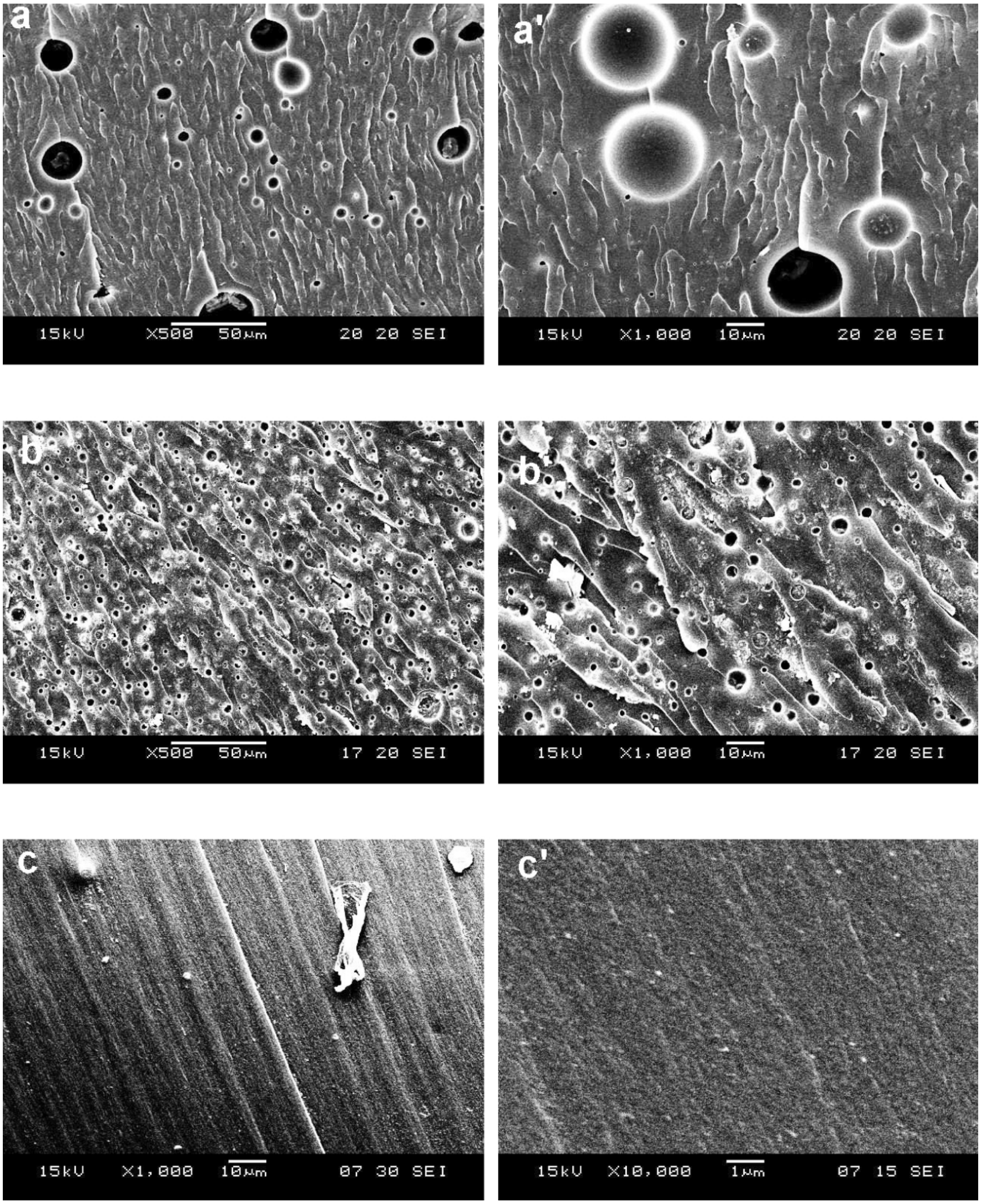

Fig. 5. SEM micrographys of the fracture surface of toughened epoxy resin networks extracted with chloroform, containing 10 wt% of (a) HTPB and the block copolymers (b) CPBER and (c) NCOPBER. (The micrographs in the right correspond to the same (a′) HTPB and the block copolymers (b′) CPBER and (c′) NCOPBER taken at higher magnifications).

3.5. Dynamic mechanical properties

Fig. 7 presents the dynamic mechanical loss factor (tan δ) versus temperature of for pure ER (Fig. 7(A)) and ER networks modified with 10% of HTPB (Fig. 7(B)) and 10% of HTPB in the form of the block copolymers NCOPBER (Fig. 7(C)) and CPBER (Fig. 7(D)). The net resin (curve A) shows a peak at around 120 °C, which is clearly related to the glass transition of the ER. The presence of HTPB or the block copolymers (NCOPBER or CTPBER) resulted only in

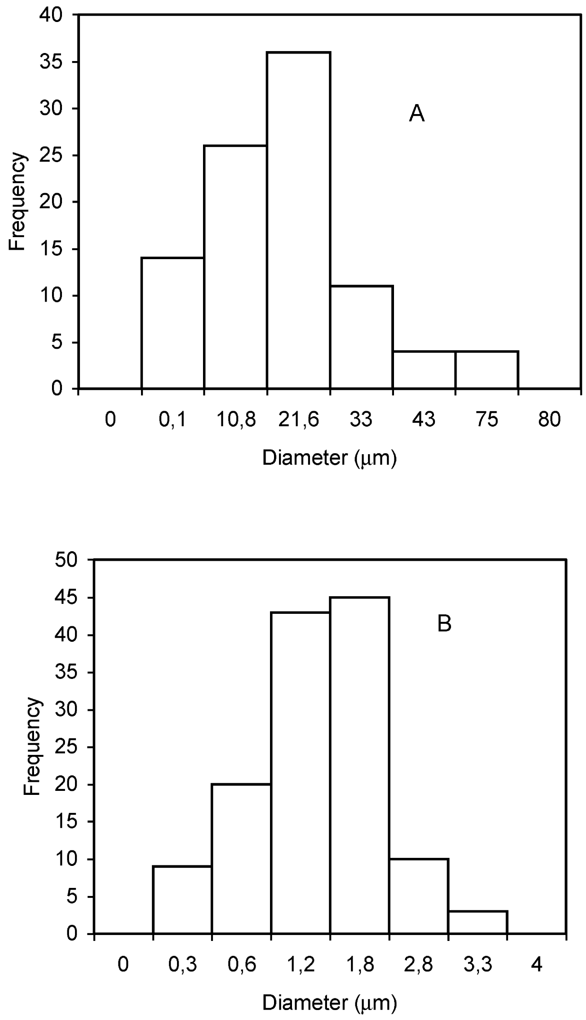

Fig. 6. Particle size distribution for epoxy resin toughened with 10 wt% of (A) HTPB and (B) the block copolymer CPBER.

a slight displacement of this transition peak towards lower temperature.

The low temperature transition peaks are shown in Fig. 8. The pure epoxy network presents a transition around −40 °C related to the epoxy resin β relaxation. This transition appears in the same region of the glass transition related to the polybutadiene phase. Regarding the rubber-modified networks, one can only observe a small displacement of this transition towards lower temperatures. Therefore, it is impossible by this technique to distinguish the relaxation related to the polybutadiene phase. However, considering that the transition at higher temperature does not present a substantial displacement towards lower temperature, even in the case of NCPBER-modified resin (Fig. 7(C)), one can assume that in all modified networks there is a phase separation. This results associated to the morphological behavior observed by SEM suggest that the rubber particles in the NCOPBER-modified epoxy resin are not totally dissolved inside the epoxy matrix but the domain size is too small (in nano-scale range) to be scattered by the light or be observed by SEM.

4. Conclusions

Epoxy networks have been modified with block copolymers prepared by pre-reacting functionalized polybutadiene with the epoxy resin. Both block copolymers prepared from isocianate end-capped HTPB or carboxyl end-capped HTPB resulted in faster gelation time as compared to the neat epoxy resin or that modified with HTPB. The system containing NCOPBER displayed the fastest gelation time probably because of the presence of urethane groups, which participate in the cure process. In this case, the cure process of the epoxy matrix takes place before the coalescence

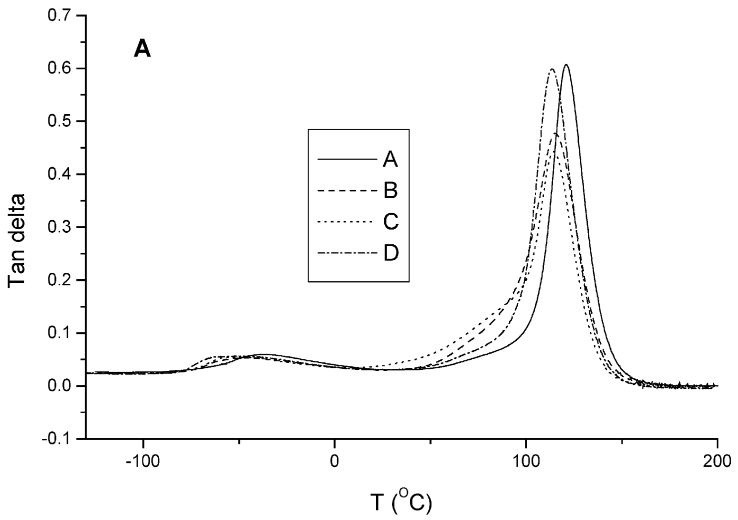

Fig. 7. Dynamic mechanical loss factor of (A) net epoxy resin and those modified with (B) HTPB, (C) NCOPBER and (D) CPBER. (All modified resins contain 10% of rubber).

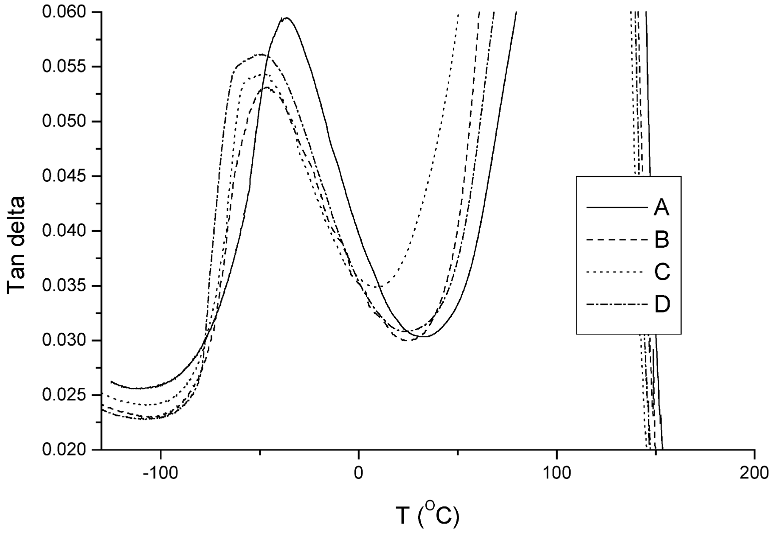

Fig. 8. Low-temperature transition of (A) net epoxy resin and those modified with (B) HTPB, (C) NCOPBER and (D) CPBER. (All modified resins contain 10% of rubber).

between the rubber particles, giving rise to clear and homogeneous material.

Epoxy network modified with CPBER displays two phase-separated morphology with very small particle size and narrow particle size distribution, as compared to epoxy-HTPB system. In that system, a toughening effect is observed as indicated by the best impact performance associated to improved flexural properties, because of the presence of rubber particles homogeneously dispersed inside the epoxy matrix.

According to the DMTA results, there is no significant variation of glass transition temperature of the epoxy matrix with the addition of HTPB or the corresponding block copolymer, which suggest that there is no dissolved rubber inside the epoxy matrix. The optical clarity observed in NCOPBER network may be due to the presence of rubber domains of very small particle size. Additional experiments based on atomic force microscopy and dielectric analysis are being performed in order to confirm the phase interaction between the phases and also the nano-scale domain size of the NCOPBER network, and will be presented in forcoming paper.

To summarize, to achieve good mechanical properties and impact resistance, the polybutadiene particles must be well adhered to the epoxy matrix. This may be achieved by pre-reacting the epoxy resin with functionalized polybutadiene, thus forming a block copolymer. The different procedure to prepare this block copolymer exerts strong influence on the morphology and on the mechanical behavior.

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