Modification of Epoxy Resin by Isocyanate-Terminated Polybutadiene

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Received 9 September 2000; accepted 8 May 2001

ABSTRACT: Hydroxy-terminated polybutadiene was functionalized with isocyanate groups and employed in preparation of a block copolymer of polybutadiene and bisphenol A diglycidyl ether (DGEBA)-based epoxy resin. The block copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy and size-exclusion chromatography (SEC). Cured blends of epoxy resin and hydroxy-terminated polybutadiene (HTPB) or a corresponding block copolymer were characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA), and scanning electron microscopy (SEM). All modified epoxy resin networks presented improved impact resistance with the addition of the rubber component at a proportion up to 10 wt % when compared to the neat cured resin. The modification with HTPB resulted in milky cured materials with phase-separated morphology. Epoxy resin blends with the block copolymer resulted in cured transparent and flexible materials with outstanding impact resistance and lower glass transition temperatures. No phase separation was discernible in blends with the block copolymer. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 838–849, 2002

Key words: thermosets; modification; polybutadiene; toughness

INTRODUCTION

Epoxy resins are known to present excellent mechanical properties such as stiffness and strength, creep resistance, and chemical resistance, resulting in excellent materials for coatings, adhesives, composites, etc. However, they also display poor crack resistance and impact resistance. The addition of rubber as a second phase to the epoxy resins has been extensively employed to increase the toughness of the brittle matrix.[1–5] In general, most of these toughening agents are low molecular liquid rubbers containing reactive end groups. By using liquid rubber, the viscosity of the resin does not increase excessively and a good mixing system can be obtained. Most of the studies on toughening epoxy resins (ERs) involve the use of functionalized butadiene–acrylonitrile copolymers with carboxyl (CTBN) or amine end groups (ATBN).[6–10] These copolymers are miscible with the ER and form a single-phase solution with the uncured resin but become immiscible as the molecular weights increase during cure.

According to several authors,[3–7] an effective toughening mechanism is reached when the rubber modifier, which is soluble in the resin, precipitates before gelation of the resin. The cured resin contains fine precipitate rubbery particles which

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Contract grant sponsor: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq); Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES); CEPG-UFRJ; FAPERJ; PETROFLEX Ind. Com. Ltda.

Contract grant sponsor: PADCT/CNPq; contract grant number: 620132/98-1.

Journal of Applied Polymer Science, Vol. 83, 838–849 (2002)

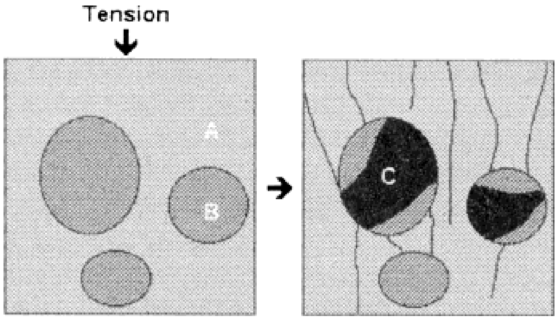

Figure 1 Schematic representation of the dissipation of tension in rubber-modified ER.

impart an enhanced resistance to crack propagation and impact strength.[11] The tensions applied in the cured epoxy matrix (A) are dissipated by the elastomer particles (B) which act as an initiation site for the plastic shear deformation of the matrix. Cavitation of the rubbery particles provides an additional dissipation of energy because the voids (C) produced during cavitation originate at points of the concentration of tension.[11–14] The process of the dissipation of tension in rubber-modified ER and the formation of voids are illustrated in Figure 1. When the modifiers remain fully miscible with the resin, they will act as flexibilizers. In these cases, the rubber modifiers do not produce a second phase and the process of dissipation and propagation of fracture is different. The dissolved rubber increases the matrix ductility and reduces the level of stress at which shear bands initiate. This phenomenon normally takes place when the reactivity of the functional groups is too high.[15]

In addition to the formation of fine precipitate rubbery particles before the gelation of the resin, the presence of a strong interfacial bond between the particles and matrix is also very important to achieve improved toughness. In the case of CTBN and ATBN, the carboxyl and amine groups react easily with the oxirane rings of the ER, thus promoting a good interfacial adhesion between the phases. In some reports in the literature, the CTBN was prereacted with the ER before adding the hardener, in order to form an epoxy-terminated elastomer molecule.[16–19] The epoxide end-capped carboxyl-terminated butadiene–acrylonitrile copolymer (ETBN) participates in the polymerization with the diamine, leading to rubber-rich domains covalently bonded to the matrix.

Hydroxy-terminated liquid polybutadiene (HTPB) can also be employed as a rubbery modifier of ERs. The main drawback of this elastomer is its poor compatibility with the resin.[20] Some authors have epoxidized HTPB mainly to increase its polarity and, hence, its compatibility with the ER.[15,21,22] The functionalization of HTPB with carboxyl groups has also been performed to improve the compatibility between the rubber particles and the matrix and to impart a good interfacial adhesion by promoting a chemical reaction between the phases.[20,23]

The aim of this article was to prepare an epoxide end-capped HTPB and to study the influence of this new compound on the properties of the cured ER matrix. For this purpose, HTPB was first reacted with an appropriate amount of toluene diisocyanate (TDI). The isocyanate end-capped HTPB (ITPB) was reacted with the ER to form a block copolymer such as illustrated in Figure 2. The isocyanate chemistry was also employed by several authors to improve the precure miscibility or to achieve more stable dispersed particles of diol compounds during the preparation of polymer networks based on ER.[24,25] Isocyanate-terminated HTPB has been also used for the toughening of vinyl ester resins.[26,27] The synthesis of the block copolymer composed of HTPB as the middle segment end-capped with two segments of the ER and its use in epoxy-cured network systems has not been well explored and constitutes a profitable route for the development of thermoset materials with impact resistance, flexibility, and good transparence.

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol A (DGEBA)-based ER used in all experiments was EPON 828, an ER based on DGEBA with an $\bar{M}_n$ of 380 and an epoxide equivalent of 192 equiv/g as determined by acid titration. The cure agent was EPICURE 3140, a mixture of amines with a number of amine groups corresponding to 378 equiv/g. Both the ER and the curing agent are produced by Shell Chemical Co. and was kindly supplied by Shell do Brasil S.A. (São Paulo, Brazil). HTPB (trade name Liquiflex H, kindly supplied by Petroflex Ind. Com., Rio de Janeiro, Brasil) presents a number-average molecular weight of 3000 and a hydroxyl number of 0.8 meq/g. Toluene diisocyanate (TDI), kindly supplied by Bayer do Brasil (Rio de Janeiro, Brasil), is composed of a mixture of 2,4- and 2,6-isomers in a proportion of

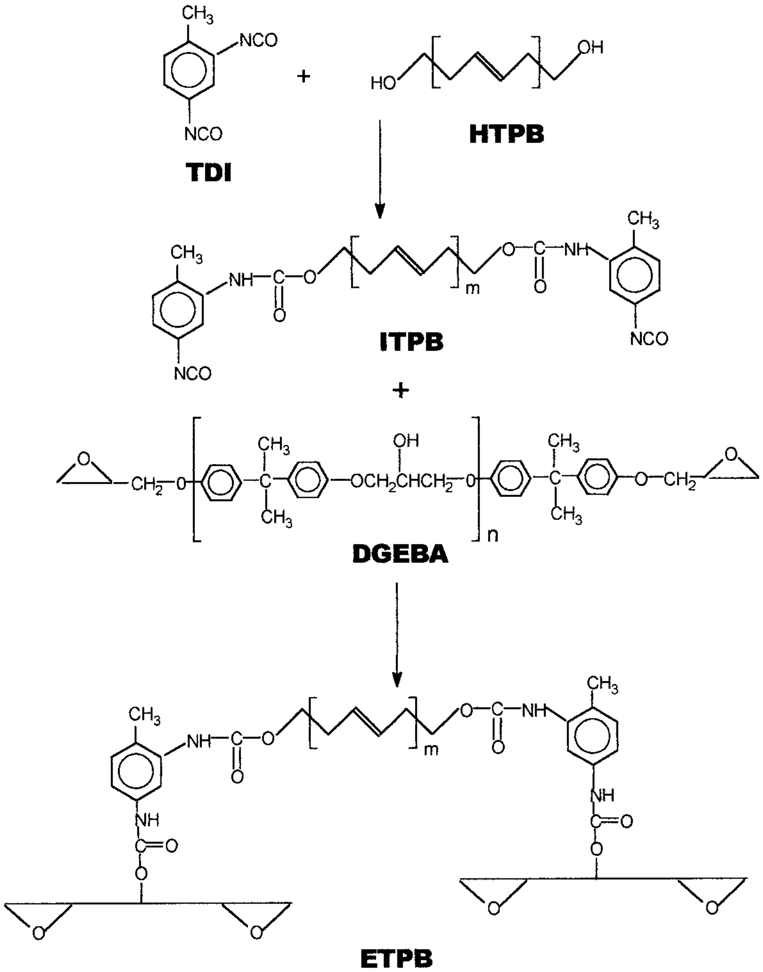

Figure 2 Synthetic steps involved in the preparation of ETPB.

80:20 wt %. All polymers were dried under a vacuum for 24 h before use.

Preparation of Isocyanate End-capped HTPB (ITPB)

The functionalization of HTPB with isocyanate groups was performed according to the literature,[26] by reacting HTPB with a small excess of TDI related to the amount of OH groups in the HTPB, in the presence of dibutyltin dilaurate (DBTDL) as a catalyst, to assure the modification of all OH groups. The reaction was performed at 80°C for 2 h with magnetic stirring under a nitrogen atmosphere. After the reaction, quantitative aliquots were withdrawn from the medium and the amount of NCO groups in the sample was determined by titration with di-*n*-butylamine, according to ASTM D1638. Additionally, an ITPB sample was put into methanol and stirred overnight at room temperature to transform all NCO groups into carbamate. This procedure was used for the size-exclusion chromatography (SEC) analysis.

Preparation of Epoxide End-capped HTPB (ETPB)

The block copolymers, as illustrated in Figure 2, were obtained by reacting ITPB with the ER. An appropriated amount of the ITPB sample (5, 10, or 15 wt %) previously prepared was added to the ER. The reaction was carried in bulk in the presence of DBTDL as a catalyst at 80°C for 2 h, using magnetic stirring and a nitrogen atmosphere. At the completion of the end-capping reaction, a small amount of the mixture was taken out for measuring the NCO content, the number-average molecular weight ($\bar{M}_n$), and the molecular weight distribution (MWD) of the end-capped HTPB. The $\bar{M}_n$ and MWD were determined by SEC (Waters 600E).

Curing Procedure

The ER was modified by HTPB or ETPB. All network polymers were prepared from stoichiometric mixtures of the ER and the hardener. Epoxy/HTPB samples (EP/HTPB) were prepared in the following typical manner: 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. Then, the curing agent, EPICURE 3140, was added and gently stirred for about 5 min to ensure proper dispersion of the hardener. The resulting homogeneous mixture was degassed for 10 min and poured into appropriated molds for the mechanical testing. The cure was performed at 100°C for 2 h.

Epoxy/ETPB samples (EP/ETPB) were prepared by mixing the ETPB sample previously obtained (containing an excess of nonreacted ER) with the EPICURE 3140. The mixture was degassed for 10 min at 70°C and poured into the molds. The curing process was performed under the same conditions employed for the EP/HTPB samples.

Characterization

The molecular weight of the uncured materials was determined by SEC in a Waters 600E HPLC equipped with a 410 ultraviolet (UV) detector, a 910 refractive index (RI) detector, and Ultrastyragel columns (50-, 100-, and 500-Å pore size). The experiments were carried out in tetrahydrofuran (THF) as an eluent with a flow rate of 1 mL/min.

Fourier transform infrared (FTIR) analysis was performed on a Perkin–Elmer 1720 spectrometer, at a 2-cm^{-1} resolution averaged over 20 scans. 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 a dynamic mode at 10°C/min under nitrogen.

The gel point was determined by putting about 100 mg of the sample in several tubes which were placed into an oil bath at a constant temperature. The tubes were withdrawn from the bath at different times and chilled in an ice bath to quench the reaction. The polymeric material was then treated with THF. The gelation point was determined from the presence of an insoluble fraction.

Dynamic mechanical analysis (DMTA) was performed using a Rheometric Scientific MK3 DMTA in the single-cantilever mode at 3 Hz and a heating rate of 5°C/min. The samples were rectangular bars 2.0 mm thick.

Scanning electron microscopy (SEM) of the neat ER was performed using a JEOL JSM-5300 SEM, using an acceleration power of 20 kV, and of the modified ER, in a Zeiss. The fracture surface after the impact test was coated with a thin layer of gold before analyzing.

Mechanical Testing

Flexural tests were performed using an Instron 4002 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 impact strength of the notched specimens was determined by using a Charpy Monsanto tensiometer, employing rectangular specimens of 50 × 10 × 5 mm, according to ASTM D-256. The tests were carried out at room temperature.

RESULTS AND DISCUSSION

Characterization of the End-capped HTPB

As illustrated in Figure 2, HTPB was first reacted with TDI in excess to produce ITPB. These functional groups react with the hydroxyl groups of the ER, thus forming ETPB. The resulting ETPB product may be considered as an A–B–A-type block copolymer in which the polybutadiene segment constitutes the middle part of the chain and the ER segments constitute the end of the block copolymer. Since the hydroxyl group of the ER is located in the middle of the chain, the resulting block copolymer contains four epoxide end groups (see Fig. 2).

The functionalization of HTPB with isocyanate groups and the formation of the block copolymer were followed by FTIR and SEC analysis. Figure 3 compares the FTIR spectra of the functionalized products (ITPB and ETPB) with the HTPB and pure ER. The spectrum of HTPB displays a characteristic absorption peak at ≈3500 cm^{-1} (peak a) due to OH stretching vibrations. The pure ER also presents this absorption (peak a), indicating the presence of free hydroxyl group in the resin sample. In addition, one can assign other characteristic peaks at 1250 cm^{-1} (peak b), related to aromatic ether; at 910 cm^{-1} (peak c), related to the

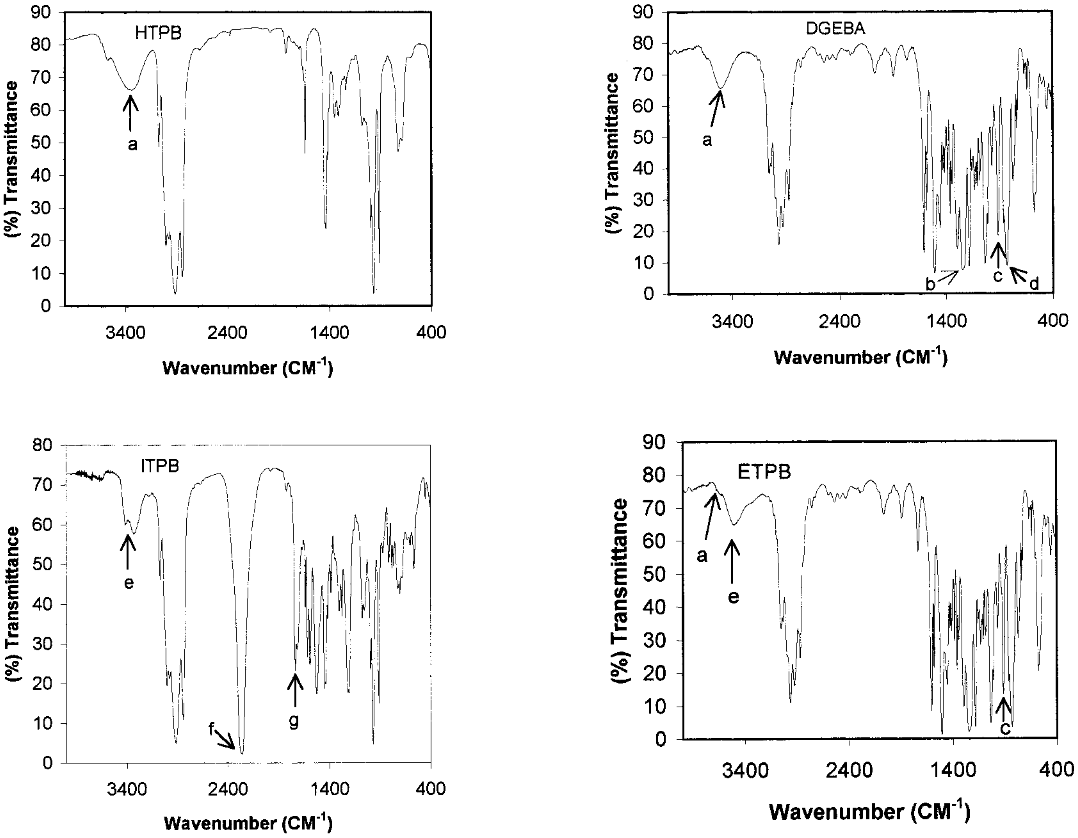

Figure 3 FTIR spectra of HTPB, pure ER (DGEBA), and functionalized products ITPB and the block copolymer (ETPB).

oxirane ring; and at 830 cm^{-1} (peak d), related to the p-phenylene groups.

The functionalization of HTPB with TDI (ITPB spectrum) resulted in the disappearance of the peak at ≈3500 cm^{-1}, indicating that the OH groups of HTPB were completely reacted with TDI. Some other new peaks appeared, confirming the reaction between HTPB and TDI. Indeed, one can observe in the ITPB spectrum the presence of absorptions at 3330–3057 cm^{-1} (peak e), characteristic of urethane groups; at 2265 cm^{-1} (peak f), related to the isocyanate groups; and at 1735 cm^{-1} (peak g), related to the carbonyl stretching of the urethane group.

By reacting ITPB with the ER, the absorption at 2265 cm^{-1}, related to the isocyanate group, disappeared, confirming the formation of the block copolymer (ETPB spectrum). In addition, some other characteristic peaks due to the ER segments can be observed, such as at 910 cm^{-1} (peak c), related to the oxirane ring. In the spectrum of the ETPB block copolymer, in addition to the presence of the absorption at 3330–3057 cm^{-1} (peak e), characteristic of urethane groups, there is also a small peak at ≈3500 cm^{-1} (peak a), indicating that the OH groups of the ER were not completely consumed by the ITPB.

SEC analysis is also a powerful tool for characterizing the functionalization of HTPB and the formation of the block copolymer. For such investigations, the presence of both refractive index (RI) and ultraviolet (UV) detectors is necessary. Pure HTPB cannot be detected by the UV detector because there is no chromophore groups in the structure. It is only detected by the RI detector. By introducing the aromatic ring through the functionalization with TDI, the resulting ITPB can be absorbed by the UV light and, consequently, be detected in the UV detector. Figure 4 compares the SEC chromatograms of ITPB, pure ER, and a block copolymer sample (ETPB). These chromatograms were obtained from the UV detector.

The ITPB sample is visible in the UV detector, indicating the success of the functionalization. The molecular weight of this compound is similar to that found for the HTPB sample used in the functionalization reaction, confirming that the HTPB was end-capped with an isocyanate group and no considerable coupling reaction between the ITPB and some HTPB molecules has taken place. The three peaks of lower molecular weight in the ITPB chromatogram can be attributed to the nonreacted TDI or some end-capped HTPB fraction of very low molecular weight.

The chromatogram of pure ER displays four peaks: According to the literature,[28] the lowest molecular weight peak ($\bar{M}_n$ around 340) is related to the ER with $n = 0$ (see Fig. 2). The other peaks in the range of molecular weights between 400 and 1300 are assigned to ER with $n > 0$.

The chromatogram of the block copolymer (ETPB) presents the characteristic peaks of both ER and ITPB. It is important to emphasize that this chromatogram can be better attributed to the block copolymer (ETPB) together with nonreacted ER than to a physical mixture of ER and ITPB. Indeed, the peaks related to the ER with $n > 0$ decreases significantly, indicating that these epoxy fractions have been reacted with ITPB. The peak corresponding to the molecular weight of 340 did not change as expected, because this fraction does not contain OH groups and, consequently, cannot react with the isocyanate group of ITPB. The peak profile corresponding to the highest molecular weight fraction is quite different from that observed in the ITPB sample, confirming the formation of the block copolymer, according to the scheme presented in Figure 2.

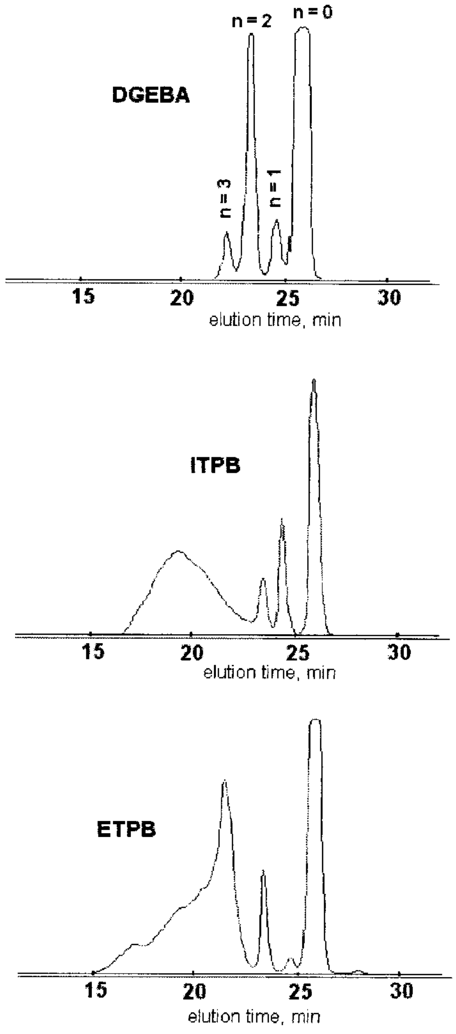

Figure 4 SEC chromatograms of pure ER (DGEBA) and functionalized products ITPB and the block copolymer (ETPB) (obtained from UV detector).

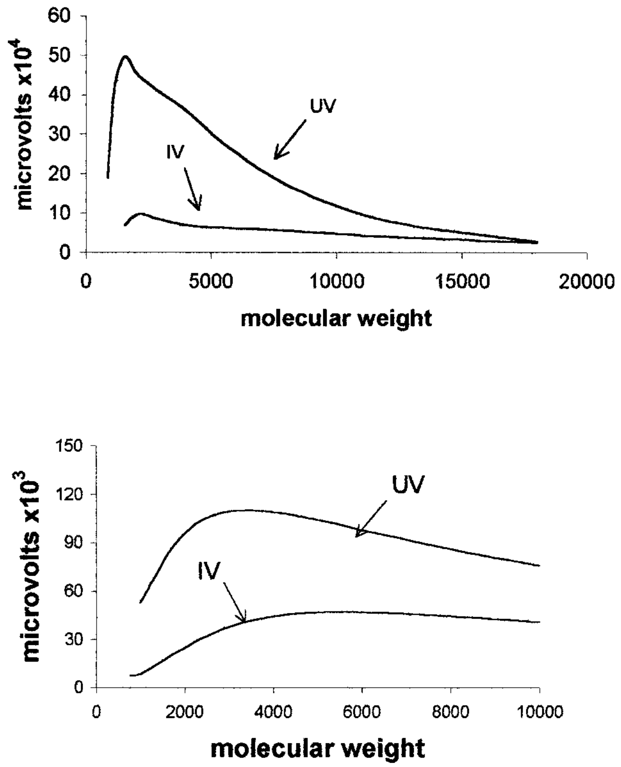

Figure 5 Chromatographic curves obtained from RI and UV detectors as a function of the molecular weight for ITPB and the block copolymer (ETPB) containing 10 wt % of ITPB.

The signals in microvolts of the chromatograms of ITPB and the block copolymer (ETPB), obtained from both the RI and UV detectors, are related to the molecular weight in Figure 5. The difference between the UV and RI signals for the ETPB is higher in the range of molecular weights between 1500–2000. In increasing the molecular weight, the intensity of the RI signal remains constant, but the intensity related to the UV signal decreases considerably. This behavior indicates that the functionality distribution of ITPB is not homogeneous. Fractions of high molecular weight display a lower amount of the isocyanate group. Consequently, they are able to incorporate a lesser amount of ER. Previous studies concerning the functionality distribution of HTPB by using a similar SEC technique revealed also an heterogeneous distribution of OH groups in the HTPB chain.[29] The fraction of higher molecular weight displayed very low functionality. Therefore, a low amount of isocyanate groups and, consequently, a low amount of the ER can be incorporated into these fractions, giving rise to a UV signal of decreased intensity.

Evaluation of the Cure Parameters

The cure parameters were evaluated by DSC analysis and by determining the time necessary to produce the minimum amount of insoluble material (gel time). These results are summarized in Table I for pure ER and the modified systems with HTPB and ETPB. The ΔH values were determined from the area of the exotherm peak taken in the dynamic mode. Figure 6 illustrates the DSC curves for pure ER, obtained in the dynamic mode. The exotherm peak related to the curing process appears during the first heating run but is completely absent during the second heating cycle. This behavior was also observed in the other rubber-modified epoxy systems listed in Table I and suggests that the cure reached practically total conversion at these conditions. However, total conversion is always impossible to reach due to steric restrictions. Oyanguren and Williams associated this result to error during the calorimetric determination.[30] The presence of HTPB or the block copolymer (ETPB) did not affect significantly the ΔH values, indicating no influence on the crosslinking degree.

Table I Curing Parameters of Pure ER and Those Rubber-Modified

ER (%)	HTPB (%)	ETPB^a (%)	ΔH^b(J/g)	Gel Time (s)
100	0	0	290	225
95	5	0	280	225
90	10	0	280	225
95	0	5	285	165
90	0	10	285	165

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

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

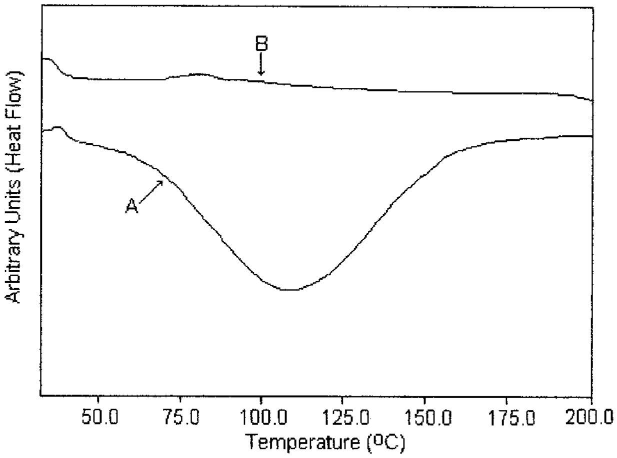

Figure 6 DSC thermograms of the ER–EPICURE reaction in the dynamic mode.

The gel time was the same when pure ER or HTPB-modified ER was submitted to the reaction with the hardener. In the case of ETPB, the gel time decreased considerably. It is important to point out that the block copolymer (ETPB) contains urethane groups. Although the amine groups of the ERICURE 3140 are more effective curing agents, the presence of the urethane groups in the block copolymer could also participate in the curing process, accelerating the formation of the insoluble material. In addition, the block copolymer ETPB contains four oxirane groups per chain, whereas the DGEBA sample contains only two oxirane groups. The presence of a higher amount of oxirane groups per chain in the block copolymer may favor network formation in less time. DSC studies performed in the static mode at 100°C revealed that almost all curing processes happened before 30–40 min (see Fig. 7).

To confirm the optimum time to reach a good extent of crosslinking, we prepared samples cured for 30 and 120 min. The specimens were analyzed by DMTA, whose results are illustrated in Figure 8. The storage modulus (E') was not influenced by the cure time. However, the damping (tan δ) and the glass transition temperature (T_g) of the epoxy matrix presented important changes. Increasing the curing time resulted in a decrease of damping and an increase of the T_g, indicating a decrease of

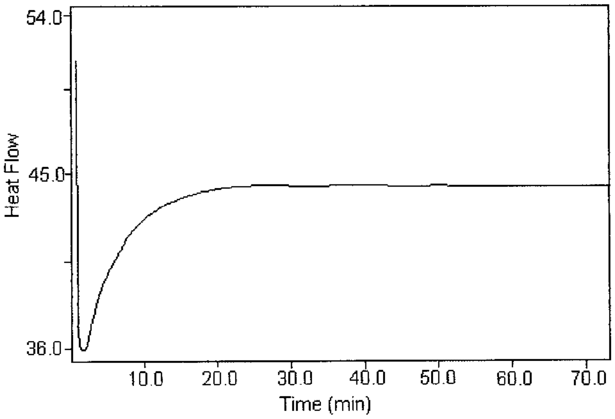

Figure 7 DSC thermogram of the ER–EPICURE reaction in the static mode at 100°C.

the chain mobility, which can be attributed to an increase of the curing degree. In spite of the DSC analysis indicating that 30–40 min should be enough time to achieve a high level of crosslinking, the DMTA results revealed that it is better to perform the curing process for a longer time. Therefore, the curing conditions as 100°C for 120 min for all samples were chosen to prepare the specimens for mechanical testing.

Mechanical Properties

The impact strength and flexural properties of the cured ER samples containing different proportions of HTPB or ETPB are summarized in Table II. In both cases, the impact strength increases with the presence of the rubber component. When the rubber component is a part of the block copolymer (ETPB), a good impact performance was achieved even with 5% of the rubber phase. With 15% of rubber, the impact strength decreased in both systems. A maximum value of the impact strength with the addition of 10 phr of epoxidized HTPB was also observed by Latha et al.[22]

The flexural modulus and flexural yield stress decrease with the addition of rubber. The decreasing of the modulus is more pronounced in ETPB-modified ER, indicating a higher flexibilizing effect of the rubber component when it takes part of the block copolymer chain. The stress versus strain curves obtained from the flexural tests are compared in Figure 9. The modification of the ER with HTPB resulted in a decrease of both the flexural yield stress and the deformation at break. Increasing the amount of rubber (15 wt %) decreased the flexural properties, probably due to gross phase separation at this composition. In spite of the lower modulus and lower yield stress, the presence of ETPB resulted in an increase of the elongation at break. By using 15% of ETPB (curve 5), the highest elongation was achieved. A decrease of the modulus associated with an increasing of the impact strength can be attributed to a flexibilization process. This process is more effective by using the epoxide-modified HTPB be-

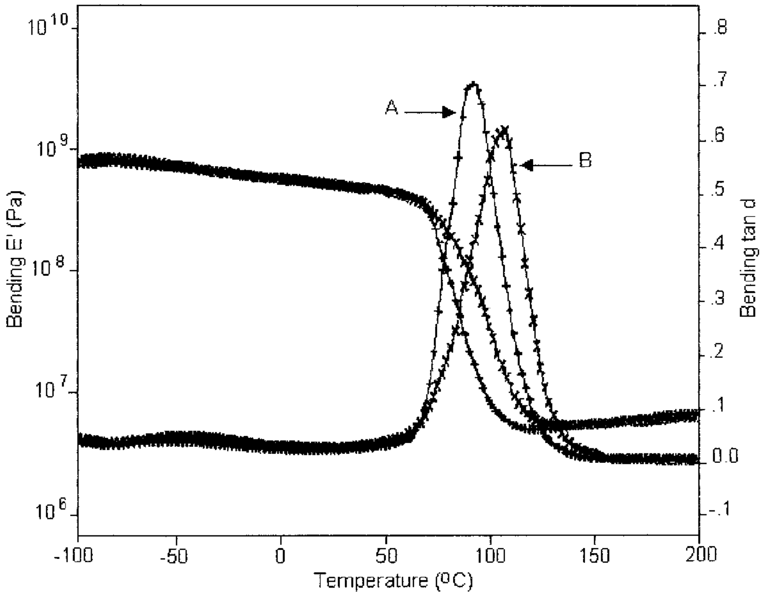

Figure 8 Dynamic mechanical analysis of ER cured at 100°C for (a) 30 min and (b) 120 min.

Table II Mechanical Properties of Cured ER Samples

ER (%)	HTPB (%)	ETPB[a] (%)	Impact Strength (J/m^2)	Flexural Yield Stress (MPa)	Flexural Modulus (MPa)
100	0	0	9.7 ± 0.4	83.8	2536
95	5	0	11.4 ± 0.3	72.0	2385
90	10	0	14.2 ± 0.4	62.2	1912
85	15	0	11.2 ± 0.4	60.0	1860
95	0	5	13.6 ± 0.3	67.0	1753
90	0	10	15.3 ± 0.4	70.0	1776
85	0	15	9.0 ± 0.9	62.3	1523

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

cause of an increased miscibility of this component into the epoxy matrix.

Dynamic Mechanical Properties

DMTA analysis was performed to investigate the influence of the rubber component on the properties of the epoxy matrix. Figure 10 compares the dynamic mechanical loss curves for cured ER containing 0, 5, and 10 wt % of HTPB. The neat resin shows a peak at 120°C, which is clearly related to the glass transition of the ER. The addition of 5 wt % of HTPB resulted in an increase of damping and a broadening of the tan δ versus temperature curve. By increasing the amount of rubber into the epoxy matrix, there is a decrease in the peak height, suggesting that the blend with 10 wt % of rubber undergoes phase separation during cure.

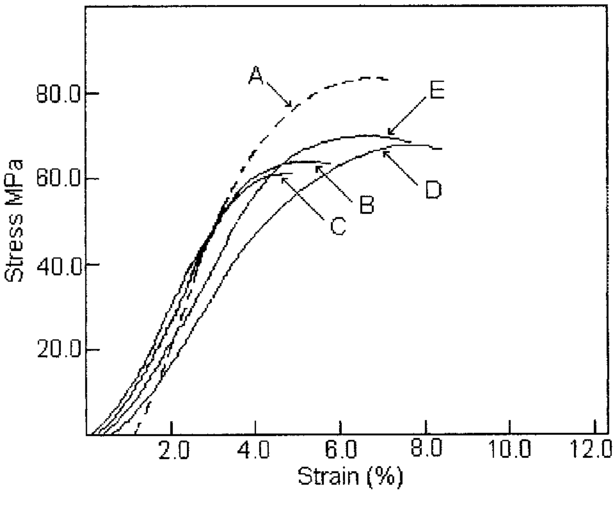

Figure 9 Stress versus strain curves obtained from flexural tests for (A) pure epoxy resin, HTPB-modified epoxy resin containing (B) 5 wt % and (C) 10 wt % of rubber, and ETPB-modified epoxy resin containing (D) 5 wt % and (E) 10 wt % of rubber.

The dynamic mechanical loss curves of cured ER modified with the ETPB block copolymer are illustrated in Figure 11. In this case, the presence of 5 or 10 wt % of the rubber phase resulted in a decrease of the transition temperature of the epoxy matrix, indicating that the rubber component in the form of a block copolymer acts as a flexibilizer for the epoxy matrix. The damping values were not substantially affected by the presence of the rubber, which is also an indication that the rubber phase is intermixed in the epoxy matrix.

Appearance and Morphology of the Cured Resins

Cured ERs modified with HTPB are milky, whereas those modified with the ETPB block copolymer are visually transparent and homogeneous, similar to the neat ER, indicating no apparent phase separation in the latter case. This feature is in agreement with the results concerning DMTA analysis.

The fractured surfaces of the modified epoxy cured networks were examined by SEM to provide further evidence of the morphological aspect across the sample thickness. Figure 12 compares the SEM micrographs of the fractured surface of the neat ER and those modified with 10 wt % of HTPB or ETPB after the impact test. The neat ER displays fractures characteristic of a brittle material, with several fissures oriented in different directions [see Fig. 12(a)]. The ER modified with 10 wt % of HTPB shows distinct separated particles of rubber, indicating an heterogeneous system [see Fig. 12(b)]. One can also distinguish several multiple fractures in the form of steady

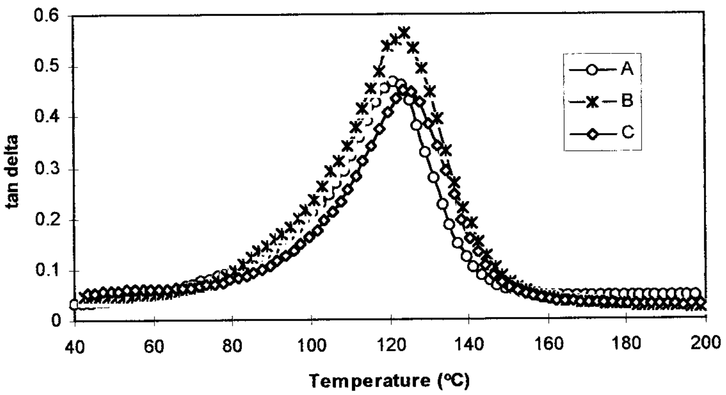

Figure 10 Dynamic mechanical spectra of (a) neat resin and mixtures containing (b) 5 wt % and (c) 10 wt % of HTPB.

tear lines whose propagation is hindered by the rubber particles situated on the path of the fracture propagation. There is also a brighter phase boundary surrounding the rubber particles which may be due to some interactions between the epoxy matrix and the rubber component.

To investigate the nature of these interactions, the cured sample was ground and submitted to extraction of the rubber phase with toluene. The extraction process was able to remove all the HTPB component present in the sample, confirming that the interactions between the epoxy matrix and the rubber particles are physical in nature. Such interactions were probably originated from hydrogen bonding between the hydroxyl groups of the HTPB and the epoxy matrix. Although the rubber particles are not chemically bonded to the epoxy matrix, this morphological situation provides a good dissipation of tension during the impact test and may be responsible for an improved toughening and impact performance of this material when compared to the neat cured ER.

Concerning the epoxy-cured system modified with the ETPB block copolymer, the fractured surface was homogeneous, demonstrating no discernible phase separation within the resolution limit of SEM [see Fig. 12(c)]. This cured sample was also ground and submitted to extraction of the rubber phase. After 2 days of treatment with toluene, no polymer material could be extracted, indicating that the block copolymer takes part of the network. Since the rubber component is in the form of a block copolymer, the coalescence between the rubber phase during the curing process is avoided and the domains cannot be observable by SEM. The morphology of the fracture looks like long fissures, indicating that the material is able to support high plastic deformation. The morphology of the sample indicates that the block copolymer acts as a flexibilizer for the ER. This result

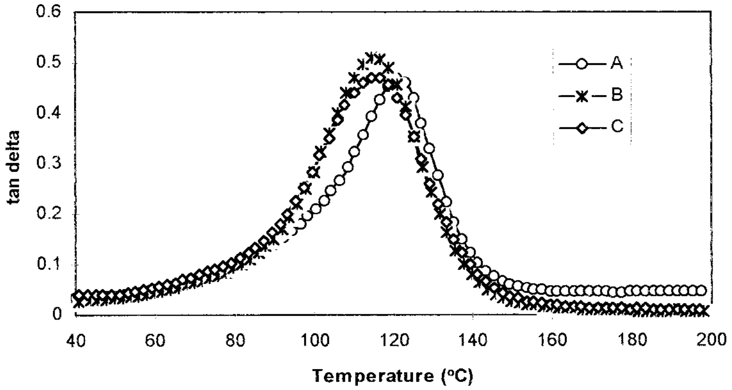

Figure 11 Dynamic mechanical spectra of (a) neat resin and mixtures containing (b) 5 wt % and (c) 10 wt % of rubber component in the form of the ETPB block copolymer.

is in agreement with the lower flexural modulus of these materials.

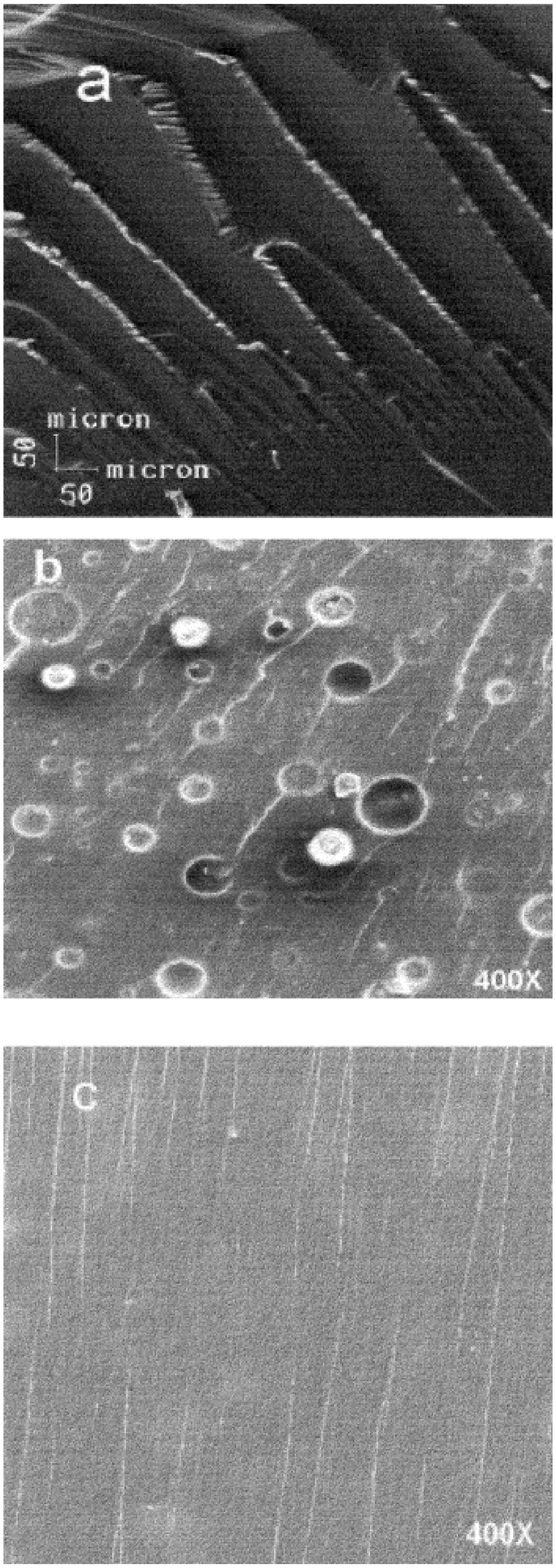

Figure 12 SEM micrographs of cured (a) neat ER and mixtures containing (b) 10 wt % of HTPB and (c) 10 wt % of rubber component in the form of the ETPB block copolymer.

CONCLUSIONS

Blends of HTPB and ER were developed. These blends presented an improved impact resistance over that of the neat cured ER. This system presents a phase-separated morphology with several multiple fractures in the form of steady tear lines whose propagation is hindered by the rubber particles situated on the path of the fracture propagation. The interactions between the epoxy matrix and the rubber component are physical in nature. To improve the adhesion between the rubber phase and the epoxy matrix, a block copolymer constituted of HTPB and ER was synthesized using HTPB-modified with isocyanate groups. This block copolymer was used as a rubber component in epoxy-cured networks, giving rise to transparent and homogeneous material with good impact resistance. HTPB in the form of a block copolymer acts as a flexibilizing agent, decreasing the flexural modulus and flexural yield stress and also the glass transition temperature of the epoxy matrix. The ability of the block copolymer (ETPB) in imparting good impact performance and flexibility while keeping the transparence in the ER material can be attributed to the peculiar structure of the block copolymer which keeps the oxirane reactive groups of the epoxy segments. The interaction between the block copolymer and the epoxy matrix is of a chemical nature because the orirane groups of the epoxy segments in the block copolymer also participate in the curing process.

The authors would like to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES), CERG–UFRJPADCT/CNPq (620132/98-1), FAPERJ, and PETROFLEX Ind. Com. Ltda. for financial support for this project.

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