

Toughening of an Epoxy Resin with an Isocyanate-Terminated Polyether

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ABSTRACT: A low-molar-mass, hydroxyl-terminated polyether [polypropylene glycol/poly(ethylene glycol) copolymer (POPE)] was functionalized with isocyanate groups and used to improve the impact resistance of a diglycidyl ether of bisphenol A based epoxy resin cured with triethylene tetramine (TETA). The effect of polyether-based modifiers (with and without NCO groups) on the curing rate of the epoxy/TETA system was investigated with rheological techniques. The NCO-functionalized polyether reduced the gel time, and this indicated an accelerating effect of the curing process. In addition, a significant improvement in the impact resistance was observed with

only a slightly detrimental effect on the stiffness and mechanical strength. Scanning electron microscopy of the corresponding epoxy network revealed a homogeneous morphology with no phase separation. The miscibility of NCO-modified POPE and the epoxy resin was also confirmed with atomic force microscopy. The glass-transition temperature of the epoxy networks was also investigated with dynamic mechanical techniques. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 159–166, 2008

Key words: curing of polymers; morphology; networks; polyethers; rheology; toughness

INTRODUCTION

Epoxy resins (ERs) are important thermosetting polymers that are widely used in structural adhesives, composites, and surface coatings.¹ The major drawback of these materials is their poor toughness in the cure state. The addition of a reactive liquid rubber such as a carboxyl-terminated butadiene–acrylonitrile copolymer is the usual way of improving the impact resistance of these materials.^{2–4} The rubber forms a single-phase solution and undergoes partial phase separation during the cure. The carboxyl groups of the rubber react with the oxirane rings of the epoxy molecules, thus improving interfacial adhesion. The rubber particles, dispersed and bonded to the epoxy matrix, act as centers for the dissipation of mechanical energy by cavitation and

shear yielding.⁵ Consequently, an improvement in the fracture toughness is generally achieved.

Poly(ethylene oxide) (PEO) has been reported to be miscible with ER cured with aromatic amines or anhydride.^{6–10} However, when an aliphatic amine was used as the hardener, the epoxy/PEO system had a phase-separated morphology after curing.¹¹ Epoxy/triethylene tetramine (TETA) networks containing low amounts (up to 7%) of low-molar-mass PEO exhibited improved impact resistance.¹² The introduction of carboxyl groups to the end of a poly(ethylene glycol) chain gave rise to polyol-modified epoxy networks with a significant improvement in the toughness.^{13–17} Amine-terminated polyoxypropylene was also employed in epoxy systems, but the toughness enhancement of the corresponding epoxy network was lower than that observed in other rubber-containing epoxy mixtures¹⁸ and depended on the resin–hardener ratio.¹⁹

Isocyanate-terminated oligomers are also good candidates for toughening ERs because of the effective interfacial adhesion that can be achieved through the reaction between isocyanate groups of the oligomer and the hydroxyl groups of ERs. Indeed, isocyanate-terminated liquid polybutadiene was successfully employed in our laboratory as an ER modifier.^{20–23} The presence of a 10% concentration of this functionalized

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oligomer resulted in improved mechanical and adhesive properties of diglycidyl ether of bisphenol A (DGEBA) based epoxy networks. The incorporation of isocyanate groups at the end of liquid hydroxyl-terminated polybutadiene was performed through a reaction with toluene diisocyanate (TDI). TDI was also used as a coupling agent between the ER and hydroxyl-terminated butadiene–acrylonitrile copolymers.²⁴

The objective of this work was to develop an isocyanate-terminated, low-molar-mass polyether and evaluate its efficiency as an impact modifier of epoxy networks. The effect of this functionalized polyol on the mechanical, dynamic mechanical, and morphological properties of epoxy networks was also investigated.

EXPERIMENTAL

Materials

A DGEBA-based ER (DER 331) was purchased from Dow Química do Brasil (São Paulo, Brazil) and presented the following characteristics: a number-average molecular weight of 380, a viscosity of 12,000 cP, and an epoxide equivalent of 192 g/equiv. The hardener used for the curing process was TETA, which was supplied by Vetec Industria Quimica, Ltd. (Rio de Janeiro, Brazil). The polyol-based polyether (G8529) was a polypropylene glycol/poly(ethylene glycol) copolymer (POPE) supplied by Arch Química Andina, C.A. (Caracas, Venezuela), and it presented the following characteristics: a number-average molecular weight of 6000 and an average hydroxyl number of 28 mg of KOH/g. A hydrocarbon-based diluent (PL400; viscosity = 400 cP), supplied by Kolon Chemical Co., Ltd. (South Korea), and benzyl alcohol, supplied by Vetec Industria Quimica, were employed as nonreactive diluents to reduce the viscosity of the system. TDI was supplied by Bayer do Brasil (Rio de Janeiro, Brazil) and used without purification. All reagents were dried *in vacuo* for 24 h at room temperature before use.

Preparation of an isocyanate-end-capped polyether polyol (POPENCO)

The synthesis of POPENCO was performed through the reaction of 100 g of a polyether (POPE) with 14 mL of TDI at 70°C for 2 h with magnetic stirring under a nitrogen atmosphere.

Modification of the ER and curing

ER (100 parts) was prereacted with different amounts of POPENCO with tin dibutyl dioctanoate (1 part) as a catalyst. The reaction was carried out at 70°C under a nitrogen atmosphere for 4 h. The nonmodified and modified ERs were diluted with nonreactive diluents: PL400 (10 parts) and benzyl alcohol (10 parts). Then, a

stoichiometric amount of TETA based on the epoxy groups was added. After the addition of the hardener, the mixture was gently mixed, degassed *in vacuo* for 15 min, and cast into silicon molds with appropriate dimensions for tensile, impact, and dynamic mechanical testing. The cure was performed for 24 h at room temperature, and this was followed by a postcuring cycle for 4 h at 100°C.

Characterization and testing

Infrared spectra were taken on a Fourier transform infrared (FTIR) spectrometer (model 1720X, Perkin Elmer, Norwalk, CT). The polyether, POPENCO, and modified ER solutions in chloroform were spread on a KBr window, and the spectrum of the dry film was recorded.

Viscosity measurements of the uncured epoxy systems were carried out on a Brookfield model DV-II viscometer (Middleboro, MA) at a shear rate of 1 rpm at 25°C.

The rheological characterization of the systems was carried out with an Anton Par Physica MCR 301 rheometer (Graz, Austria) with parallel plates 25 mm in diameter. The oscillatory shear flow measurements were conducted under isothermal conditions. The plates were preheated to the isothermal cure temperature, and the plate spacing was zeroed. The plates were then separated, and the resin sample was rapidly inserted. The plates were then brought back together to a gap of 0.5 mm. The experiment was initiated when the system returned to the set temperature (~ 1 min). An angular frequency of 1 Hz and an amplitude of 1% were applied.

The tensile properties were measured with an Instron 5569 universal testing machine (Boston, MA) at room temperature according to ASTM D 638. The crosshead speed was 1.5 mm/min.

A dynamic mechanical analyzer (Q-800, TA Scientific, New Castle, DE) was employed to measure the dynamic mechanical properties of the cured epoxy networks at a fixed frequency of 10 Hz and a heating rate of 3°C/min. A three-point-bending clamp with a span of 20 mm was used for 25 × 10 × 2 mm³ samples.

An Izod unnotched impact test was carried out on a Ceast instrumented impact tester (a Resil model impactor) with a hammer energy corresponding to 1.5 J. At least seven specimens for each sample were used.

Scanning electron microscopy (SEM) was performed with a JEOL JSM-L5300 microscope (Tokyo, Japan) with an accelerator power of 10 kV. The samples were fractured, and the surface was coated with a thin layer of gold and analyzed with the help of a secondary electron detector.

Atomic force microscopy (AFM) (Ames, IA) was performed with a Topometrix TMS 2010 discovery

instrument equipped with a noncontact AFM probe head and a 70- μm tripot scanner. The tips (1660, Topometrix) were made of Si, with a spring constant of about 40 N/m and resonance frequencies in the range of 100–150 kHz. Scanning was carried out at the free cantilever oscillation frequency and different amplitudes, which depended on the stability and contrast obtained. The set point was fixed at 25–45% of the free oscillation amplitude.

RESULTS AND DISCUSSION

Preparation and characterization of the modified ER

The functionalization of polyol (POPE) with isocyanate groups to form POPENCO and the subsequent coupling reaction with the ER to form the block copolymer (POPENCO-ER) are illustrated in Figure 1. The modified ERs containing the POPENCO-ER block copolymer were liquid, and no gelling was observed after this pre-reaction.

Figure 2 compares the FTIR spectra of POPE, POPENCO, and the ER containing 10 phr POPENCO-ER. POPENCO displayed some characteristic absorptions that were not present in the polyether at 3300–3057 (cm^{-1} , peak a) and 1732 (cm^{-1} , peak b), which were related to the N–H and C=O bond stretching of the urethane groups, respectively, and at 2270 (cm^{-1} , peak c), which was assigned to the free NCO groups in the TDI moiety. After the reaction with the ER, the peak related to the NCO groups completely disappeared [Fig. 2(c)], and this confirmed the formation of the

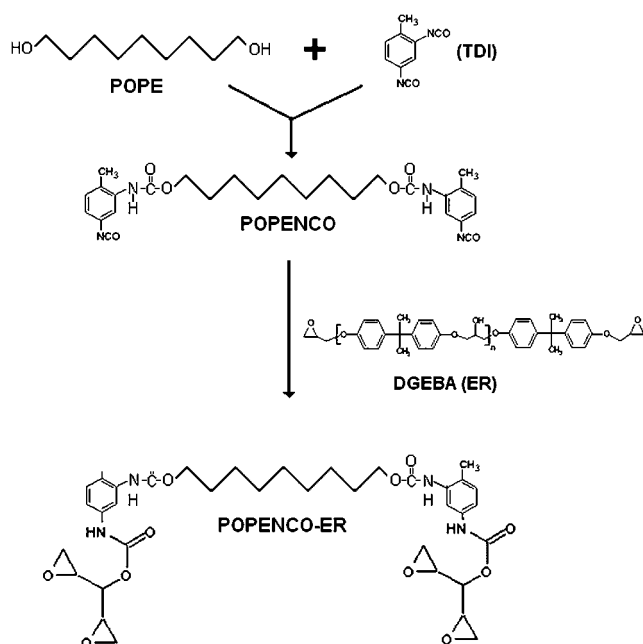


Figure 1 Scheme for the functionalization of POPE and the formation of the POPENCO-ER block copolymer.

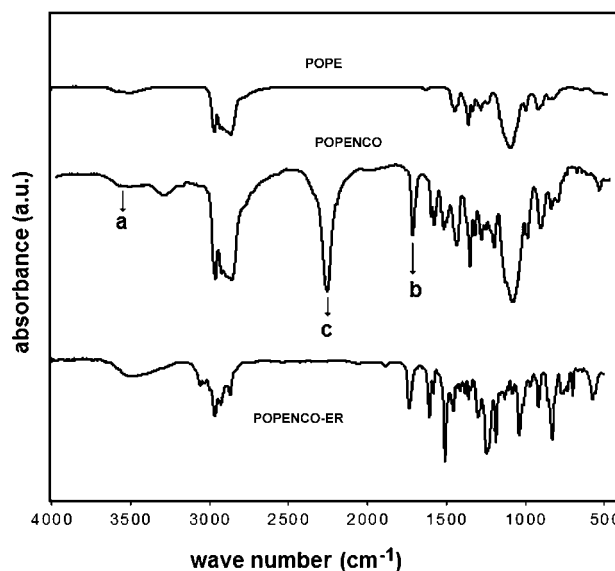


Figure 2 FTIR spectra of POPE, POPENCO, and the POPENCO-ER block copolymer.

block copolymer composed of a polyether segment end-capped with ER, as illustrated in Figure 1.

The viscosity of the modified ER was determined with a Brookfield viscometer at 25°C before the addition of the hardener. Table I presents the viscosity values as a function of the polyol content. The viscosity of the POPE/ER physical blends was slightly higher than that of pure ER and was not affected by the amount of POPE in the mixture. However, when the POPENCO-ER block copolymer was employed as the modifier, a substantial increase in the viscosity was observed, and this effect was more pronounced as the amount of POPENCO-ER increased. This result confirmed the formation of the POPENCO-ER block copolymer and could be explained by the presence of NH bonds of the urethane groups in the block copolymer, which interacted with the ER through hydrogen bonding, contributing to the increase in the viscosity.

Rheological analysis

The cure of a thermoset is a complex process because different chemical reactions are involved in it. As the cure reaction proceeds, the molar mass

TABLE I
Viscosity of the Uncured Epoxy Systems as a Function of the Modifier Content

Modifier (phr)	Viscosity (cP)	
	POPE	POPENCO-ER block copolymer
0	1,300	1,300
10	2,000	3,800
20	2,050	6,000
30	2,000	11,000

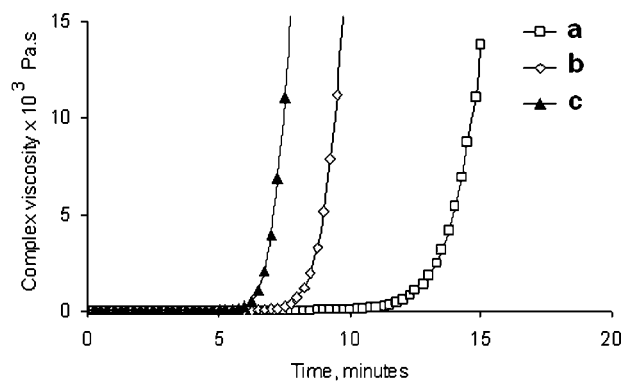


Figure 3 Viscosity versus the time under isothermal conditions: (a) neat epoxy/TETA, (b) a POPE-modified epoxy/TETA system, and (c) a POPENCO-ER modified epoxy/TETA system.

increases, and several chains link together, giving rise to the expansion of linear chains that soon start to branch and crosslink, resulting in a network of infinite molar mass.²⁵ This sudden and irreversible transformation from a viscous liquid to an elastic gel is defined as the gelation point, and the time at which it occurs, at a given isothermal cure temperature, is the gelation time. The macroscopic consequences of the gelation include a rapid approach toward infinite viscosity and the development of elastic properties not present in the pregel resin. These changes can be eas-

TABLE II
Effects of the Polyether-Based Modifier on the Gel Time of Epoxy/TETA Systems at Different Temperatures from Rheological Measurements

Matrix	Temperature (°C)	Gelation time (min)	Activation energy (kJ/mol)
Neat epoxy	70	24.1	71.5
	75	16.8	
	80	13.8	
	90	7.5	
	100	3.0	
POPE (10 phr)	70	16.3	61.1
	75	10.3	
	80	8.2	
	90	4.5	
	100	2.8	
POPENCO-ER (10 phr)	70	13.5	55.1
	75	8.1	
	80	6.4	
	90	4.3	
	100	2.6	

ily detected from rheological experiments performed under isothermal conditions.^{26–28}

The effects of polyol and POPENCO-ER on the cure characteristics of the epoxy/TETA system were evaluated with a rheometer with parallel plates. Figure 3 compares the dependence of the viscosity on time for the pure ER/TETA system and the systems modified with 10% POPE or POPENCO-ER. The gel

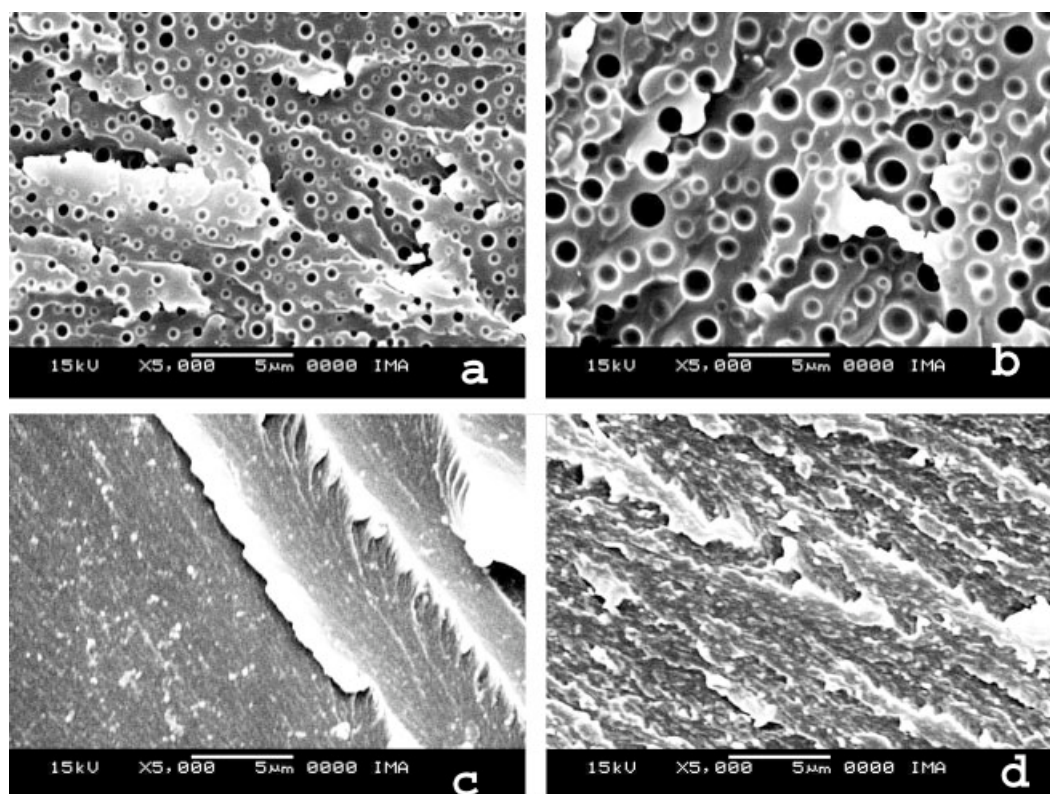


Figure 4 SEM micrographs of epoxy networks containing (a) 10 or (b) 20 phr POPE or (c) 10 or (d) 20 phr POPENCO-ER.

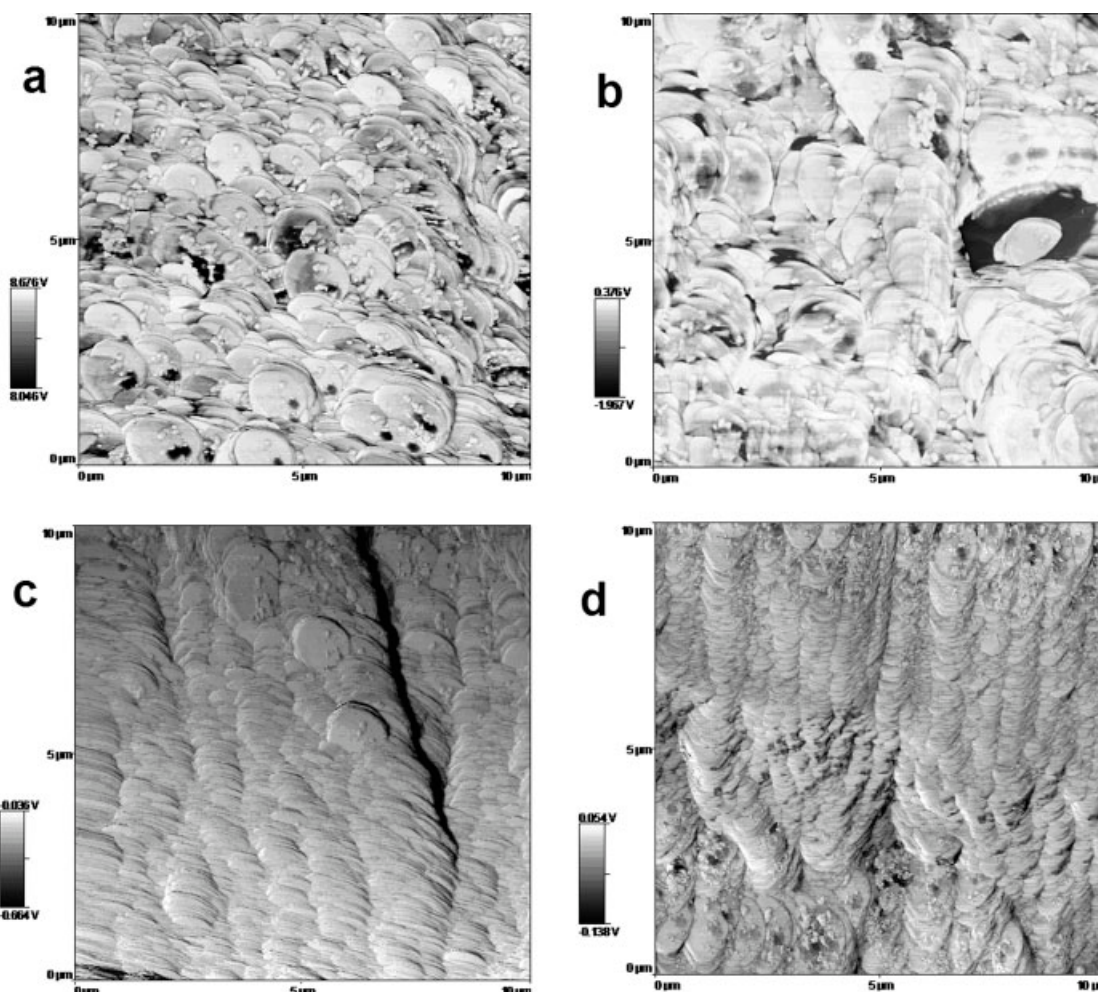


Figure 5 AFM micrographs of epoxy networks containing (a) 10 or (b) 20 phr POPE or (c) 10 or (d) 20 phr POPENCO-ER.

time was determined under isothermal conditions at different temperatures and established as the point corresponding to the crossover between the elastic and viscous modulus curves.^{29,30} The values are listed in Table II. ER modified with 10% POPE as a physical blend displayed a lower gel time than pure ER. This behavior was also observed by Bonnet et al.³¹ in some thermoplastic-modified epoxy systems and was attributed to the increased concentration of reactants in the epoxy-rich phase when thermoplastic segregation occurs.

The system containing 10 phr POPENCO-ER presented a shorter gel time than the other systems. This behavior could be attributed to a catalytic effect induced in the curing process as a result of the urethane groups, which could interact with the epoxide rings of the matrix. The urethane groups played the role of a proton donor, accelerating the reaction by hydrogen bonding with the oxirane ring and weakening the bond strength of the epoxide group.

As the temperature increased, the gel time decreased, and the difference between the modi-

fied and unmodified epoxy/TETA systems also decreased (see Table II). This fact can be explained at a microscopic level as an increase in the chain mobility with an increase in the temperature. The apparent activation energy was obtained from the slope of a logarithmic plot of the gel time versus the reciprocal absolute temperature³² and is presented in Table II. The activation energy related to the epoxy curing

TABLE III
Tensile Properties of the Epoxy Networks

Modifier (phr)	Tensile strength (MPa)		Elongation at break (%)		Young modulus (MPa)	
	A	B	A	B	A	B
0	63	63	2.4	2.4	2230	2230
10	46	48	2.4	2.7	2050	2750
20	45	24	2.1	2.1	2100	1700
30	16	22	1.4	1.8	1100	1350

A = POPE; B = POPENCO-ER.

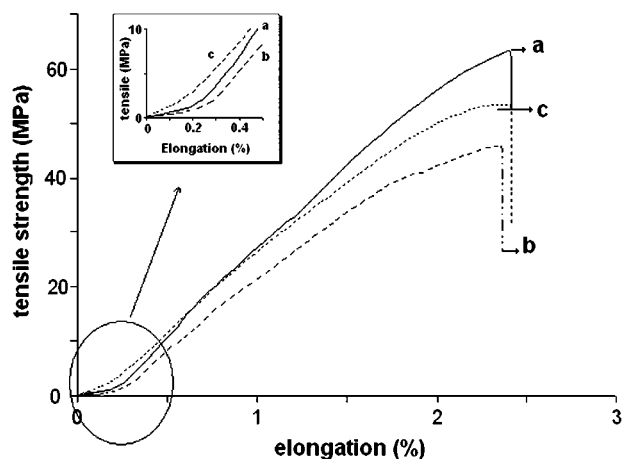


Figure 6 Stress–strain curves of epoxy networks containing (a) no modifier, (b) 10 phr POPE, or (c) 10 phr POPENCO–ER.

process was lower when POPENCO–ER was used as a modifier, and this confirmed the accelerating effect of this system.

Morphological studies

SEM micrographs of the fracture surfaces of the modified epoxy networks are shown in Figure 4. The system containing 10 phr POPE presented two distinct phases, which were characterized by small, spherical domains with a nearly uniform size (ca. 0.2–0.4 μm) quite regularly dispersed in the epoxy matrix. The domain size increased as the amount of POPE increased [Fig. 4(b)].

When the POPENCO–ER block copolymer was used as a modifier, the network morphology was homogeneous, demonstrating no discernible phase separation until a magnification of 5000 \times . In addition, the samples containing block copolymer concentrations of 10 or 20 phr appeared visually transparent and homogeneous, and this indicated that the preformed block copolymer was miscible with the epoxy matrix. This behavior demonstrates that the isocyanate-functionalized polyether improved the interfacial adhesion and reduced the chance of phase separation even during the curing process.

AFM micrographs of the epoxy networks modified with both POPE and POPEPNCO–ER are presented in Figure 5. The systems containing 10 phr POPENCO–ER did not present a phase-separated morphology, even at a higher magnification, and this confirmed the miscibility of the components on both SEM and AFM scales. Increasing the concentration of POPENCO–ER resulted in an appearance of some phase separation, but the particle size was very small [Fig. 5(d)].

Tensile and impact properties

The effect of the polyether modifiers (POPE and POPENCO–ER) on the tensile properties is summarized in Table III. The tensile strength of all the modified epoxy networks was lower than that of the unmodified epoxy network because of the presence of a low-molar-mass polyether. Among the modified systems, that containing 10 phr POPENCO–ER presented the highest values of the tensile strength and Young's modulus. Despite the lower ultimate tensile strength, this modified system presented a higher modulus than the unmodified epoxy network. This behavior is better illustrated in Figure 6, which shows that in the linear viscoelasticity region, the tensile strength was higher for the POPENCO–ER modified network, and this resulted in a higher Young's modulus. This phenomenon may be attributed to the interfacial adhesion and the probable participation of both the oxirane ring and urethane groups of the block copolymer in the network.

An instrumented impact test allows us to analyze the absorbed energy and provides designers with a guide to determine what service conditions a material can endure.³³ The total energy spent to fail a material may be separated into two parts: the crack initiation energy (work done to reach the greatest applied stress) and the propagation energy. The balance between the crack initiation energy and propagation energy gives us information about the mechanism of deformation and the energy absorption during the impact. In this work, Izod instrumented impact tests were performed with samples containing the modifier at a concentration of 10 or 20 phr because the best tensile properties were achieved

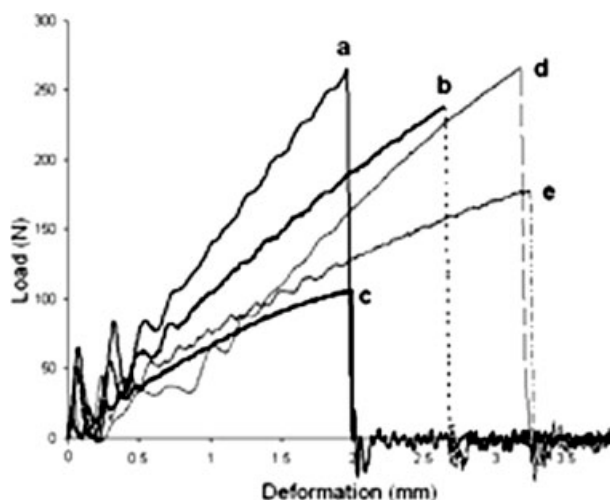


Figure 7 Dependence of the load force on the displacement of (a) non modified epoxy network, (b) epoxy network modified with 10 phr and (c) 20 phr of POPE, (d) epoxy networks modified with 10 phr, and (e) 20 phr of POPENCO–ER.

TABLE IV
Impact Properties of the Epoxy Networks

Matrix modifier	Maximum load (N)	Displacement (mm)	Total energy (J)	Impact resilience (J/m ²)
Neat epoxy	290 ± 16	1.4 ± 0.10	0.20 ± 0.05	4.0 ± 0.17
POPE (10 phr)	250 ± 19	2.7 ± 0.12	0.35 ± 0.09	5.5 ± 0.21
POPE (20 phr)	105 ± 15	1.5 ± 0.2	0.10 ± 0.05	2.2 ± 0.15
POPENCO-ER (10 phr)	285 ± 11	3.3 ± 0.15	0.40 ± 0.07	7.5 ± 0.26
POPENCO-ER (20 phr)	178 ± 13	3.3 ± 0.10	0.25 ± 0.06	5.7 ± 0.3

with these proportions. Figure 7 illustrates the dependence of the load-point force on the displacement for unmodified and modified epoxy networks containing 10 or 20 phr POPE and POPENCO-ER. The first peak in the curves is due to inertia, and the further rise in force until the highest peak is attained represents the time for crack initiation. All the epoxy systems presented practically no propagation energy because the load-point force fell sharply as soon as the crack initiated. This behavior is typical of catastrophic failure, as expected for a brittle material.

The epoxy network containing 10 phr POPE displayed a lower load-point force than the unmodified epoxy but a higher displacement, which corresponded to a larger area under the load-displacement curve, indicating a higher total fracture energy. As summarized in Table IV, the impact resilience of the unmodified epoxy matrix was 4 kJ/m², and it increased to 5.5 kJ/m² when 10 phr POPE was compounded with it; this indicated a toughening effect of the polyether, even without strong interactions. The addition of this polyether at a 20 phr concentration substantially reduced the impact resistance of the epoxy network.

The epoxy network modified with 10 phr POPENCO-ER displayed a load-point force as high as that of unmodified epoxy but the highest displacement, which corresponded to a total fracture energy of 7.5 kJ/m². These results confirmed the improvement of the toughness when the polyether was chemically bonded to the epoxy matrix. Increasing the amount of POPENCO-ER in the system resulted in a decrease in the load-point force and a displacement similar to that found for a similar system modified with 10 phr POPENCO-ER.

Viscoelastic properties of the epoxy networks

To investigate the effect of POPE and POPENCO-ER on the viscoelastic properties, the pure epoxy and modified epoxy networks were studied with dynamic mechanical analysis. Plots of tan δ and the storage modulus versus the temperature for these systems are shown in Figure 8. All the systems presented glass-transition temperatures between 75 and 85°C, which corresponded to the α transition of the epoxy matrix. These values were lower than those normally found for epoxy systems because of the presence of nonreac-

tive diluents (20 phr) acting as plasticizers. The epoxy network containing 10 phr POPE [Fig. 8(b)] displayed a slightly higher glass-transition temperature than the nonmodified epoxy, whereas the system containing 10 phr POPENCO-ER presented a transition temperature similar to that of the neat epoxy network. These results suggest that the miscibility of the system containing POPENCO-ER (observed by microscopic techniques) did not affect the glass-transition temperature, probably because of the strong interaction between the components.

At a temperature lower than the α transition, the storage modulus of the POPE-modified epoxy network was lower than that of the unmodified one, as expected, because of the presence of flexible poly-

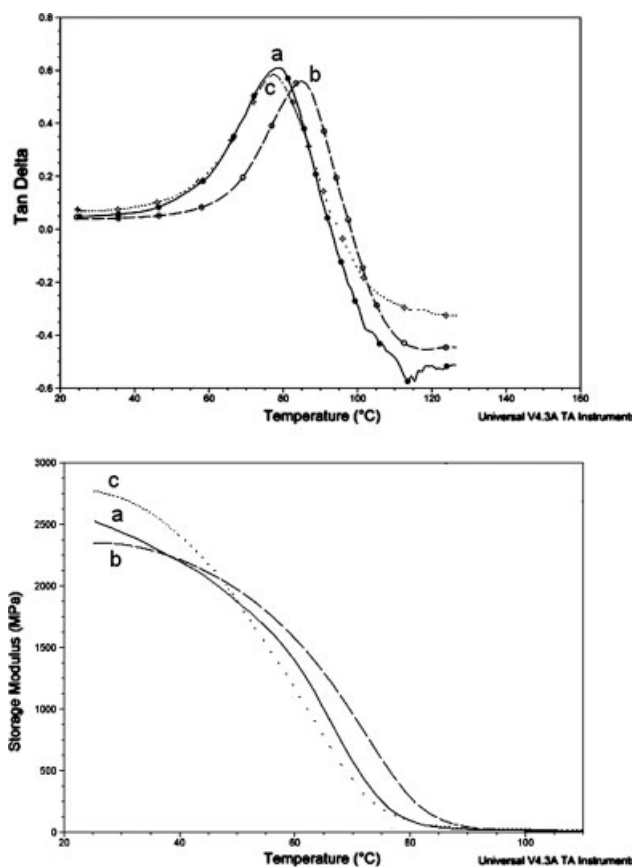


Figure 8 Dynamic mechanical parameters (tan δ and storage modulus) as functions of the temperature for epoxy networks containing (a) no modifier, (b) 10 phr POPE, or (c) 10 phr POPENCO-ER.

ether chains with a low molar mass. The storage modulus of the POPENCO-ER block copolymer modified system was higher than that of the neat epoxy network. This result is in agreement with the tensile properties and confirms the strong interaction between the components.

CONCLUSIONS

A polyether polyol functionalized with isocyanate groups was able to react with the hydroxyl groups of an ER, forming a block copolymer. This block copolymer reduced significantly the curing time of an epoxy/TETA system, and this was attributed to the catalytic effect of the urethane groups. In addition, it led to homogeneous and transparent epoxy networks with no phase separation discernible by SEM or AFM techniques. An improvement in the modulus and toughness was also achieved by the addition of 10 phr POPENCO-ER, without changes in the glass-transition temperature. These results are very promising for several applications.

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