

Polyurethane-Ductilized Epoxy Resins

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Received 18 April 1997; accepted 30 October 1997

ABSTRACT: Amine-cured epoxy resins were modified to improve their impact properties. Urethane prepolymers (PUs), in which terminal isocyanate groups were blocked with nonylphenol (NP) for easy handling, were used as modifiers. The synthesis of the elastomers were carried out at different NCO : OH ratios: 1 : 1, 2 : 1, and 3 : 1 (PU1, PU2, and PU3). Characterization of these materials by GPC and FTIR indicated that PU1 has a negligible amount of NCO-terminated chains and no unreacted toluenediisocyanate (TDI). PU2 and PU3 have free-blocked TDI in the mixture, even after distillation under a vacuum. The molecular weight and polydispersity of the prepolymer increases as $PU3 < PU2 < PU1$. Copolymerization was carried out by crosslinking with a mixture of cycloaliphatic amines, which react with the epoxy ring and with the NCO groups by deblocking and urea formation. Dynamic mechanical tests were used to measure the glass transition temperatures (T_g) of the copolymers. Two T_g were found if PU1 was the epoxy modifier, indicating that phase separation took place. This was correlated with a structure of PU1 of linear chains with a negligible amount of reactive groups. Flexural and compression properties showed negligible changes for PU2- and PU3-modified epoxy, but the critical strain energy release rate (G_{1C}) was improved if PU2 was the modifier. This behavior was explained by the linkage of elastomeric chains into the epoxy network. The PU1–epoxy copolymer showed a completely different behavior, with the bending modulus (E_b) reduced to almost one-half with respect to that of the epoxy matrix and with largely improved impact properties. This difference was attributed to the separation of an elastomeric phase, which favors the formation of shear bands in the epoxy matrix. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1781–1789, 1998

Key words: modified epoxy; urethane–epoxy copolymers; blocked urethane prepolymer; fracture

INTRODUCTION

Amine-cured epoxy resins are widely used as adhesives, protective coatings, and matrices for composite materials. However, they have a low impact resistance and are usually combined with plasti-

cizers or with an elastomeric second phase to ductilize them.

Kinloch et al.¹ studied the behavior to fracture and impact of resins of diglycidyl ether of bisphenol A (DGEBA) modified with a carboxyl-terminated butadiene–acrylonitrile copolymer (CTBN). They found that the values of the critical strain energy release rate (G_{1C}) and fracture toughness (K_{1C}) are independent of the test geometry, but they are strongly dependent on the test velocity. Moreover, they observed that G_{1C} and K_{1C} increase when the CTBN concentration increases.

Verchere et al.² studied the relation between

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Contract grant sponsor: CONICET (National Research Council of República Argentina).

Contract grant sponsor: Third World Academy of Sciences (TWAS); contract grant number: 92-001 RG/CHE/LA.

Journal of Applied Polymer Science, Vol. 68, 1781–1789 (1998)

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CCC 0021-8995/98/111781-09

the morphology and mechanical properties of epoxy resins modified by the addition of CTBN and cured with amines. In all the analyzed compositions, phase separation took place during curing and K_{1C} and G_{1C} increased, while the elastic modulus and yield stress decreased.

Geisler and Kelley³ observed a similar behavior in epoxy modified with “core shell” elastomeric inclusions. Since the separated phase was not chemically linked to the network, the glass transition temperature of the matrix was unchanged.

Hang et al.^{4,5} used an urethane prepolymer to copolymerize with an epoxy resin by direct reaction of the isocyanate with the epoxy ring. The improvement of the impact properties showed a maximum at low urethane concentrations. This behavior was the result of the balance between the effects of the addition of soft segments to the network and the increment of the crosslinking density as the urethane concentration increased.

In this work, urethane prepolymers (PUs) of different molecular weights were selected to modify the epoxy thermosets. The PUs presented different characteristics depending on the initial ratio of the raw materials (toluene diisocyanate and polyol) from the stoichiometric to the excess of isocyanate ($r = 1-3$). The terminal NCO groups were blocked with nonylphenol (NP) for easy handling of the prepolymer. The epoxy resin was copolymerized with the different PU elastomers by coreaction with a cycloaliphatic amine. Varying the copolymer composition, the thermosets of different properties were synthesized, obtaining ductilized epoxy resins. The system offers the possibility of manufacturing ductilized thermosets or PU elastomers of increased rigidity depending on the formulation of the copolymer. In this work, the highest PU concentration used was 20% by weight, that is, only the range of modified epoxy resins was studied. The relation among the formulation, structure, and final properties of the copolymers is presented in this work.

EXPERIMENTAL

Materials

The materials used for this study, their source, and main characteristics are listed in Table I. The polyol poly(propylene oxide)glycol (PPG 1000) and epoxy resin (DGEBA) were heated at 80°C and degassed under a vacuum overnight before use. The diisocyanate (TDI), catalyst (dybutyl tin

dilaurate, DBTDL), and crosslinking agent (mixture of cycloaliphatic amines, MA) were used as received.

Synthesis of Blocked Urethane Prepolymers (PU)

The reactor used in the PU synthesis is shown in the Figure 1. The preparation of the blocked urethane prepolymer was carried out in two steps: In the first step, PPG 1000 was reacted with TDI using three different NCO/OH ratios: 1, 2, and 3. The conditions of the reaction, selected from previous publications and preliminary tests⁶⁻⁹ were 70°C during 2 h under a dry nitrogen atmosphere. When a ratio of NCO/OH = 3 was used, excess TDI was partially distilled under a vacuum at 80°C during 5 h. In the second step, NP was added to react with the terminal NCO groups.

A prepolymer with a NCO/OH ratio of 2 (PU2NB) was obtained under the same conditions but the excess of TDI was totally distilled during 40 h. In this case, the prepolymer was not blocked with NP.

Epoxy-Urethane Copolymerization

The copolymers were obtained by crosslinking a DGEBA-PU mixture with MA. The schematic of the crosslinking reaction is shown in the Figure 2. The amine groups react with the epoxy groups by ring opening or with isocyanate groups by replacing the blocking agent, NP, which remains in the network.^{2,7,10} To select the cure conditions for the samples, the thermogram of the crosslinking of an epoxy-amine sample was obtained. The reaction peak has a maximum at 105°C and extends up to 150°C. The glass transition of the formed network was 130°C. To verify that the copolymerization reaction took place, a sample of the PU-MA mixture was cured at 80°C during 3 h and the product analyzed using FTIR spectroscopy. A peak at 1650 cm^{-1} appears, which corresponds to the formed urea groups,¹¹ indicating that the isocyanate deblocking reaction occurred. According to the above results, the following curing cycle was used: 1 h at 40°C, 1.5 h at 100°C, and postcure at 160°C during 6 h.

The test specimens were prepared with 0, 10, and 20% by weight of the PU in the epoxy resin. DGEBA and PU were mixed at a temperature of 70°C during 30 min, degassed, and then cooled. Finally, the amine was added, and the mixture was cast into a rectangular aluminum-Teflon mold following the cure cycle already mentioned.

Table I Materials

Designation	Description	Trade Name	Source
DGEBA	Dyglycidyl ether of bisphenol A; weight per epoxy equivalent = 198 g/eq	ARALDIT - GY 250	Ciba Geigy Co.
PPG1000	Poly(propylene oxide)glycol, weight per hydroxyl equivalent = 501 g/eq	ALKURAN 1000	Alkanos S.A. Co.
TDI	Toluene diisocyanate (80 : 20 mixture of the 2,4 : 2,6 isomers)	TDI	Petroquímica Rio Tercero Co.
NP	Nonylphenol (85% content of <i>p</i> -isomers)		Fluka
DBTDL	Dibutyl tin dilaurate		Alkanos S.A. Co.
MA	Mixture of cycloaliphatic amines, weight per amine equivalent = 59.5 g/eq		Ciba Geigy Co.

Testing Methods

The synthesis of the PUs was followed using infrared spectroscopy, using a Bruker IFS 25 FTIR spectrometer with a transmission cell and a resolution of 2 cm^{-1} . The curves are the average of 50 scans. This technique allowed detection of the characteristic peaks of isocyanate and urethane groups at different times.

Gel permeation chromatography (GPC) was used to determine the molecular weight distribution of the PUs. GPC was performed in a Waters 244 device provided with a refractive index detector. THF was used as a solvent at a 1 mL/min flowing rate. Columns of Styragel of 500, 1000, 10,000 and 100,000 Å were used.

The heat evolved during the copolymerization

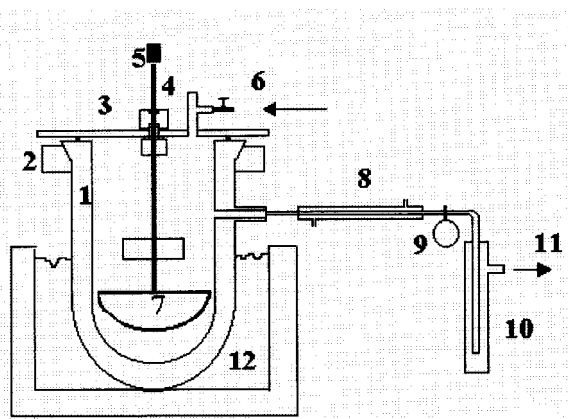


Figure 1 Reactor for the synthesis of the prepolymers: (1) glass reactor; (2) nylon ring; (3) steel cover; (4) mechanical coupling; (5) electrical motor; (6) nitrogen supply; (7) stirrer; (8) cooler; (9) flask; (10) cooling trap; (11) exit for vacuum; (12) thermostatic bath.

reaction and the glass transition temperatures taken as the onset of the transition of the final materials were determined using a differential scanning calorimeter (Shimadzu DSC 50) at a heat rate of $10^\circ\text{C}/\text{min}$. A dynamic mechanical analyzer (DMA 7, Perkin-Elmer) with a three-point bending geometry was used to determine the glass transition temperatures of the copolymers as the

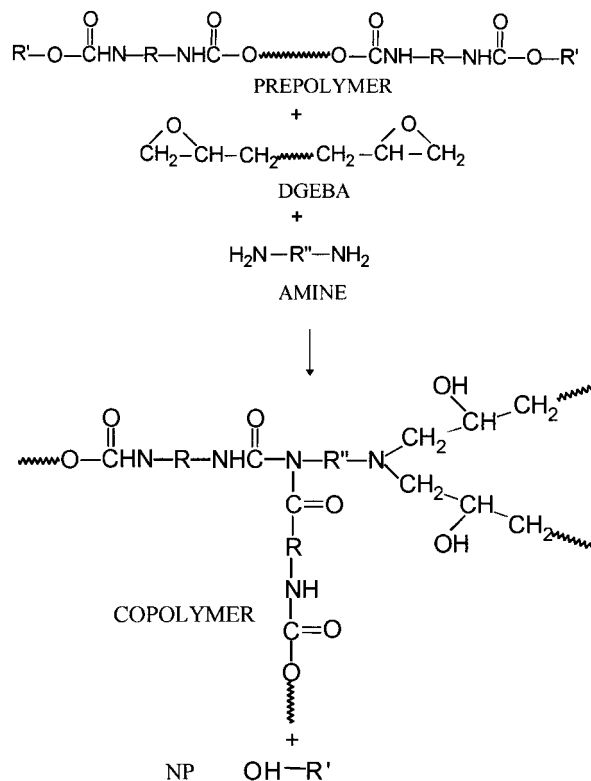


Figure 2 Schematic of the crosslinking reaction of the copolymer.

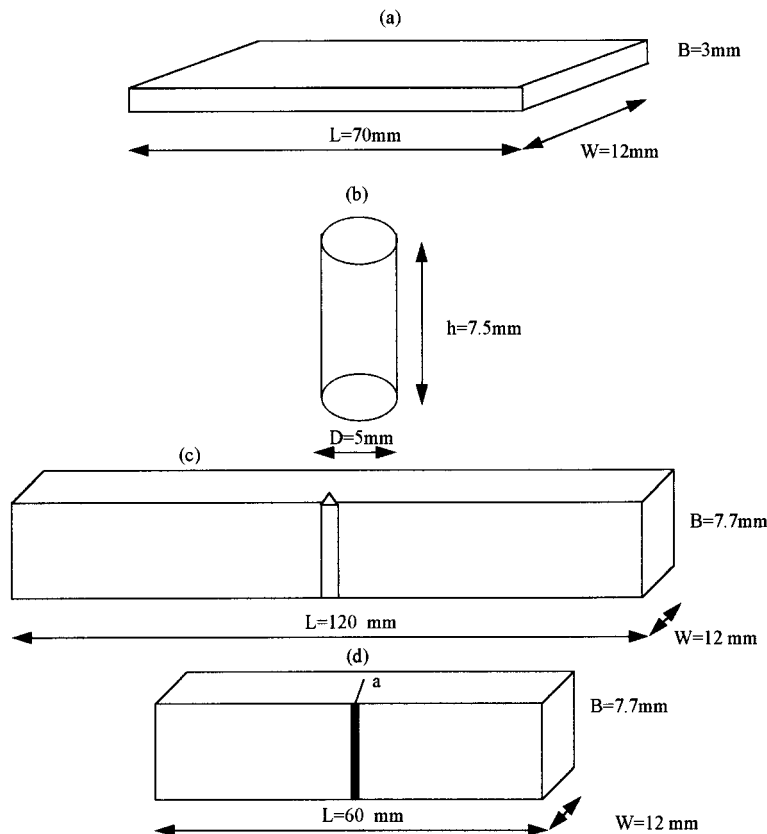


Figure 3 Geometry of the test specimens to be used in the measurement of mechanical properties: (a) bending; (b) compression; (c) impact; (d) fracture.

maximum in the $\tan \delta$ peak. The dimensions of the samples were approximately $20 \times 3 \times 1$ mm. The heat rate was $10^\circ\text{C}/\text{min}$ from -70 to 180°C and a fixed frequency of 1 Hz was used.

Bending and compressive tests were performed with a Shimadzu SC 500 universal testing machine. Bending tests were run following the procedure ASTM D790-86 (method 1, procedure A) at a crosshead speed of 12 mm/min. The compression samples were deformed between polished steel plates following the test procedure ASTM D695-91 at a crosshead speed of 0.5 mm/min. The displacements were calculated from the readings obtained with a linear variable differential transducer (LVDT). The bending and compressive tests specimens were machined to achieve the dimensions shown in the Figure 3(a,b).

The impact tests were conducted using a pendulum-striker (Wolpert, PW5). The impact resistance was determined following the norm ASTM D266-84 (method B, Charpy). The impact velocity used was 3.4 m/s. The dimensions of the test specimens are shown in the Figure 3(c).

Notched test specimens were used to determine

the critical strain energy release rate, G_{1C} [Fig. 3(d)]. Sharp initial cracks were obtained by first machining a V-notch of 1 mm and then generating a natural crack by carefully tapping on a new razor blade placed in the notch of the precompressed specimen. G_{1C} were determined using the following equation:

$$G_{1C} = U/BW\phi \quad (1)$$

where U is the stored elastic strain energy in the specimen at the onset of crack growth; W , the width; B , the thickness of the specimen; and ϕ , a dimensionless factor, which depends on the a/W and L/W ratios, where a is the initial length of a sharp crack and L is the span of the test specimen between supports. The values of ϕ were calculated from previous publications.¹²⁻¹⁴ The values of U were determined by the direct reading of the angle of the pendulum, α , calculated from the following calibration:

$$U = mgl(\sin \alpha - \sin \alpha') \quad (2)$$

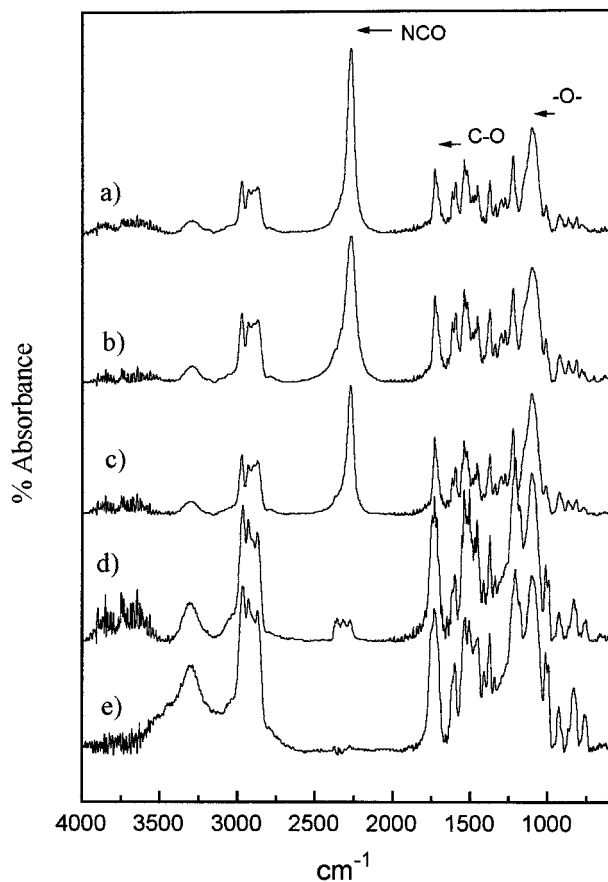


Figure 4 FTIR spectra of the synthesis of PU3. First step: (a) 0 h; (b) 2 h; (c) after TDI distillation. Second step: (d) 0 h; (e) 2 h.

where m and l are the mass and the length of the pendulum respectively; and α' , the angle without the sample. The impact velocity used, in this case, was 0.95 m/s. The ratio a/W varies between 0.08 and 0.7. The length of the initial crack was determined after performing the test using a profile projector (10 \times) to observe the surface of the broken samples. A five-point average was used to calculate the initial crack length.

RESULTS AND DISCUSSION

Characterization of Blocked Urethane Prepolymers (PU)

The PU synthesis was followed by FTIR. A sample of the reacting mixture was taken every 2 h. The progress of the reaction in the PU3 synthesis was indicated by the reduction of the NCO (2275 cm^{-1}) absorption peak and the increment of the C=O (1733 cm^{-1}) absorption peak [Fig. 4(a,b)].

Then, the TDI in excess was partially distilled during 5 h [Fig. 4(c)]. During the second step [Fig. 4(d,e)], the NCO peak is reduced and disappeared completely after NP blocking. The same behavior was observed for PU2. The NCO group concentration at the end of the first step of the PU1 synthesis (Fig. 5) is negligible, which was expected at complete conversion (NCO/OH = 1).

All blocked prepolymers were analyzed by GPC. The corresponding chromatograms of the blocked prepolymers are shown in the Figure 6(a–c). As the NCO/OH ratio increases, the average molecular weight of the urethane polymer fraction decreases and its distribution is narrower.

An assignment of the peaks was realized to identify the major chemical structures in the prepolymers. For this purpose, a blocked PU of a NCO/OH ratio of 10 was analyzed by GPC [Fig. 6(e)]. This material contains mainly blocked TDI and blocked prepolymer, originating from one TDI-terminated glycol. The peaks appeared at elution times of 37.45, 40.10, and 42.2 min and were assigned to the blocked prepolymer, blocked TDI, and NP, respectively. The chromatograms of PU3 and PU2 showed these three peaks, but broad peaks were observed at 36 min for PU3 and at 31.6 min for PU2. The chains that leave the column at these elution times have larger molecular weights and have structures that contained more than one glycol. PU3 and especially PU2

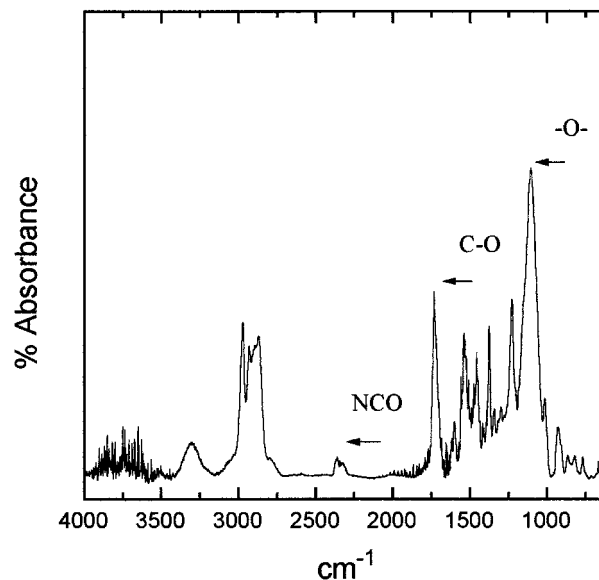


Figure 5 FTIR spectra of the synthesis of PU1, 2 h (end of first step).

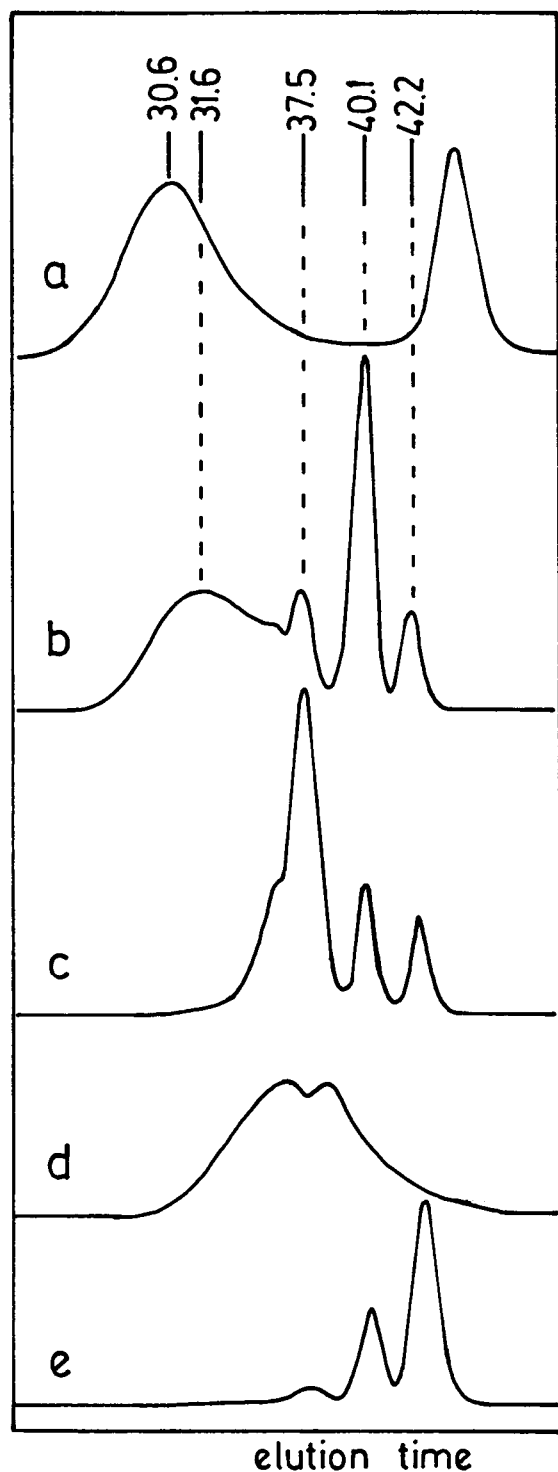


Figure 6 GPC chromatograms of prepolymers: (a) PU1; (b) PU2; (c) PU3; (d) PU2NB; (e) PU10.

chromatograms show that an important amount of blocked TDI remains in the final product.

The PU2NB chromatogram [Fig. 6(d)] shows an intermediate distribution of molecular weights

between the PU3 and PU2, with no peak corresponding to excess TDI. The PU1 chromatogram does not show the peak of blocked TDI, confirming the observation made by FTIR spectroscopy.

To complete the characterization, a polystyrene calibration was used to determine the molecular weights of the polymeric fraction of the urethanes. Results are shown in Table II.

Copolymers: Thermal Properties

A dynamic mechanical analyzer and a differential scanning calorimeter were used to determine the glass transition temperatures of the copolymers. As shown in Table III, a single glass transition was detected by DMA if PU2 or PU3 was used as the modifier. However, while the PU3 copolymers are transparent, the PU2 copolymers are slightly translucent, thus an incipient phase separation cannot be discarded in this case. As the concentration of PU3 or PU2 increases, the T_g decreases slightly. Instead, when PU1 was used as the modifier, two glass transitions were observed by DMA at -38 and 137°C corresponding to the elastomer and epoxy phase, respectively, indicating that phase separation took place. The concentration of terminal NCO groups in PU1 is negligible; thus, the chains of PU1 do not form part of the network, or at least they become dangling chains, which phase separate during curing. The similar values of the glass transition temperatures of the epoxy matrix of the PU1 copolymer and that of the pure epoxy (137 and 135°C , respectively) indicate that there are no PU1 chains diluted in the epoxy phase of the copolymer. Similar behavior has been reported by other authors.^{2,3}

The different behavior of copolymers formed with PU3 or PU2 is related to their chemical structures. GPC and FTIR indicate that these materials have two major structures: prepolymer and blocked TDI. The final thermoset consists of cross-linking points (amine) joined by the epoxy resin, TDI, or the prepolymer. The isocyanate increases the rigidity of the epoxy-amine network, while the urethane prepolymer ductilizes it. The experimental data are the result of those two opposite effects. Thus, the glass transition temperature of the copolymer made with PU2-20% (115 and 98°C , DMA and DSC respectively), is higher than that of the copolymer made with PU3-20% (111 and 92°C). These results cannot be explained if only the elastomeric contribution is taken into account. Since PU2 has a larger molecular weight, a lower T_g was initially expected.

Table II Average Molecular Weight of the Prepolymer by PS Calibration

Prepolymer	NCO/OH Molar Ratio	A		B	
		M_n	M_w	M_n	M_w
PU1	0.996	5978	40268		
PU2	1.977	1823	13952	6741	21480
PU3	3.037	1978	3256	2866	3764
PU2NB	2.008	829	4911		

B is the polymeric fraction in the prepolymers (the contribution of the blocked TDI is considered in column A).

The increase of T_g due to the presence of blocked TDI in the prepolymer was further confirmed by using PU2NB as the modifier. This prepolymer has not blocked TDI; thus, the only expected effect on the T_g is a decrease due to the coreaction of the elastomeric chains with the epoxy. The measured T_g (85°C) of the copolymer confirms the above explanation.

Mechanical Properties

The flexural modulus (E_b), compression yield stress (σ_c), impact resistance (IR), and critical strain energy release rate (G_{1C}) were determined for all the copolymers. The results are shown in Table III. The compression stress versus strain and U versus $BW\phi$ curves for copolymers with 20% of PU1, PU2, PU2NB, and PU3 and for pure epoxy are shown in the Figures 7 and 8, respectively.

If PU2, PU3, or PU2NB are used as modifiers, the impact resistance increases slightly as the percentage of the prepolymers increases while the changes in compressive yield stress and flexural

modulus are negligible. The critical strain energy release rate increases only for the copolymers with PU2 or PU2NB (see Table III, Figs. 7 and 8). The slight improvement in the impact properties with respect to that of the epoxy-amine system can be explained for the linkage of urethane elastomeric segments into the network.

When PU1 is used as the modifier, the critical energy release rate and impact resistance increase with the percentage of PU1, but the bending modulus and compressive yield stress strongly decrease (compressive yield stress drops from 113 MPa in pure epoxy to 46 MPa in the copolymer). These last effects are an unavoidable disadvantage if a large improvement in the impact properties is required. The most probable reason for the improved impact properties was discussed by Yee and Pearson¹⁵ and Kinloch et al.,^{16,17} who proposed that shear yielding is the main mechanism for energy dissipation during the plastic deformation of an epoxy-amine network. As was previously explained, the low concentration of terminal NCO groups and the high molecular weight of the PU1 chains promote the formation of a sep-

Table III Mechanical and Thermal Properties of the Final Materials

Samples	E_b (GPa)	σ_c (MPa)	IR (J/m)	G_{1C} (kJ/m ²)	T_g (°C) DSC	T_g (°C) (tan δ)
Epoxy	2.8 ± 0.17	113 ± 7	12.8 ± 1.9	0.456 ± 0.014	130	135
PU1-10%		100 ± 2	21.2 ± 2.2	0.584 ± 0.009	134	150
PU1-20%	1.48 ± 0.2	46 ± 3	26.5 ± 1	1.677 ± 0.034	131	137 and -38
PU2-10%	2.71 ± 0.19		13.1 ± 0.6		120	100 to 120
PU2-20%	2.70 ± 0.1	96 ± 3	20 ± 1.2	0.737 ± 0.015	98	115
PU3-10%		114 ± 2	16.2 ± 3.3	0.484 ± 0.013		106
PU3-20%	2.79 ± 0.1	109 ± 1	19.2 ± 3.4	0.452 ± 0.018	92	111
PU2NB-15.6%		106 ± 2	16.8 ± 3.5	0.581 ± 0.009	85	
NP-Ep ^a		118 ± 1	15.2 ± 4	0.481 ± 0.007	130	

Bending and impact properties were measured at room temperature.

^a Crosslinked epoxy resin containing 5.4% by weight of nonlyphenol.

arate phase during the curing. Therefore, the inclusion of an elastomeric phase favors the formation of shear bands in the epoxy matrix and holes (cavitation) at high test velocities, both of them increasing the toughness of the network.

The effect of the residual NP on the impact properties was determined by preparing a sample of crosslinked epoxy containing an amount of NP similar to that remaining in the PU2-epoxy copolymer (5.4% by weight). In the quantity used, the presence of NP did not produce variations on the impact properties of the epoxy network, as reported in Table III.

CONCLUSIONS

Urethane prepolymers of different molecular weights and molecular weight distributions were synthesized and the terminal isocyanate groups were blocked with an alkyl phenol for easy handling. As the NCO : OH ratio increases from 1 to 3, the molecular weight of the prepolymer decreases and shows a narrower distribution. Phase separation of the elastomeric phase in an epoxy matrix was detected only when PU1 was used as the modifier.

Ductilization of the epoxy network was achieved by copolymerization of the epoxy with the PUs. Use of PU1 resulted in a material with

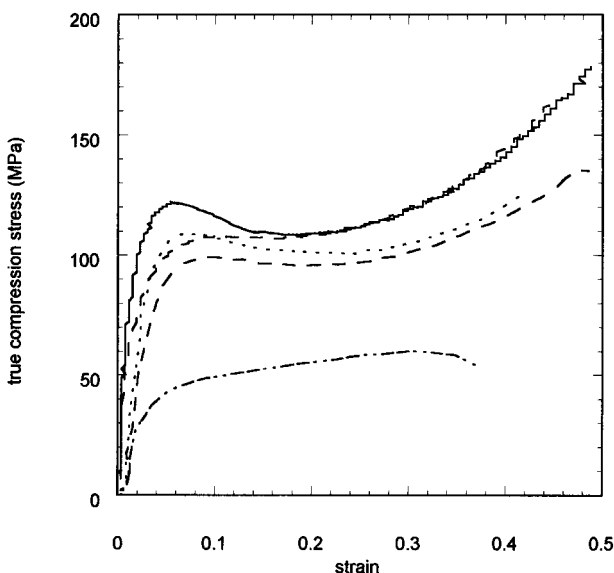


Figure 7 Compression stress-strain curves of copolymers: (—) unmodified epoxy; copolymer containing (···) 20% of PU3, (---) 20% of PU2, (- · - ·) 20% of PU1, and (- - -) 20% of PU2NB.

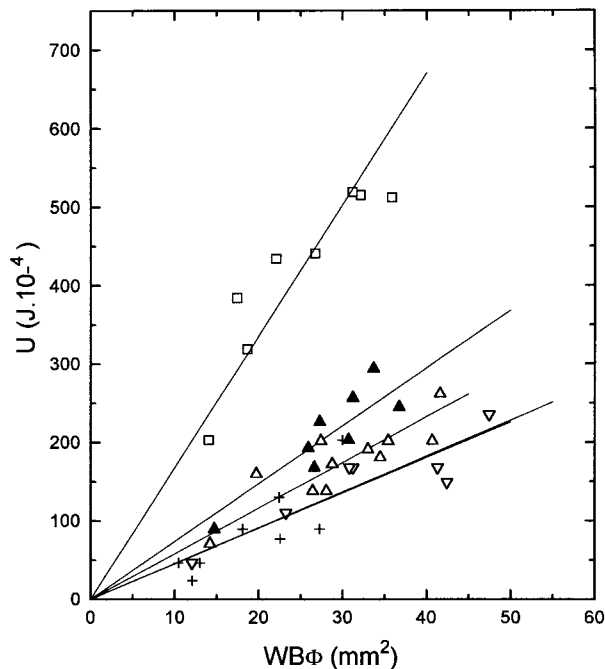


Figure 8 Impact experimental results plotted according to eq. (1) for the PU-modified epoxy specimens: (□) 20% of PU1; (▲) 20% of PU2; (+) 20% of PU3; (▽) unmodified epoxy; (△) 15.6% of PU2NB.

largely improved impact properties but a reduced flexural modulus and compression yield stress. This was related to a two-phase structure, where the urethane chains are mostly free in the epoxy matrix. The elastomeric phase promotes shear bands in the epoxy matrix, increasing its toughness. Unfortunately, this improvement in impact properties is accompanied by an unwanted large decrease in the modulus and compression yield stress. Use of PU2 gave a material with almost the same modulus and yield stress as the matrix, but with slightly better impact properties than those of the epoxy matrix. The choice of PU1 or PU2 as the modifier will depend on the final use of the copolymer.

The authors thank CONICET (National Research Council of República Argentina) for the financial support and especially for the fellowship awarded to P. M. S. Thanks are also due to the Third World Academy of Sciences (TWAS) for Research Grant No. 92-001 RG/CHE/LA. We appreciate the help of Lic. D. Fasse, who obtained the FTIR spectra. Special thanks are given to Dr. P. Frontini for his suggestions and for valuable discussions.

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