Epoxy–Urethane Copolymers: Relation Between Morphology and Properties

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ABSTRACT: The modification of an amine-cured epoxy resin by the addition of polyurethanes (PU) was investigated, and their mechanical and impact properties were related to their microstructure and morphology. For the study, two different PU were selected: a commercial sample, D12, with a NCO : OH ratio equal to 2 and end blocked by reaction with an alkylphenol; and a synthesized sample, with NCO : OH ratio equal to 1 and equally end blocked in our laboratory. The usual trend of improved toughening and reduced modulus, E_F, and compression yield stress, σ_{YC}, was observed in all samples. However, the toughening of the D12-modified samples was larger for the same initial rubber content. This result correlates with a finer rubber particle separation, but also the ductilization effect that this rubber has on the epoxy-rich phase. D12 co-reacts with the epoxy–amine, leading to a lower glass transition temperature (T_g) of the modified system and incomplete phase separation, as observed by scanning electron microscopy. The practically unreactive PU1 rubber leads to the usual spherical inclusion morphology observed in modified epoxies, except at 20% rubber content. The particular morphology generated in this case, co-continuous epoxy-rich and rubber-rich regions, leads to a material with the largest toughening in this study, but also with an impressive reduction in mechanical properties. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2544–2552, 2001

Key words: blocked urethane prepolymer; urethane–epoxy copolymers; modified epoxy; phase separation

INTRODUCTION

Elastomer-modified epoxy networks are commonly employed as adhesives, protective coatings, and matrices for composite materials. Generally, the modification of the epoxy systems is carried out by dissolving liquid elastomers in an amine–epoxy mixture that initially is homogeneous and then becomes phase separated during the polymerization reaction. The reactive mixture remains homogeneous until a certain extent of reaction is reached (cloud-point conversion). At this point, a modifier-rich phase is segregated as particles of a few micrometers in size. The competence between the phase separation process and the chemical reaction determines the morphology and properties of the final thermoset.

It is well known that an elastomer second phase increases the toughness of a brittle matrix. Many studies have been conducted to explain the effect of size and distribution of the second phase and the mechanisms of deformation associated with the improvement of the fracture toughness of the epoxy systems.[1–4] The toughening increases with the volume fraction of dispersed

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Table I   Materials

Designation	Description	Trade Name	Source
DGEBA	Dyglycidyl ether of bisphenol A. Weight per epoxy equivalent = 190 g/eq	ARALDIT—GY 9527	DISTRALTEC
PPG1000	Poly(propylen oxide)glycol Weight per hidroxyl 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 *p*-isomers)		FLUKA
DBTDL	Dibutyl tin dilaurate		ALKANOS S.A. Co.
MA	Mixture of cycloaliphatic amines Weight per amine equivalent = 59.5 g/eq		DISTRALTEC
D12	Commercial elastomer based on a linear polyurethane, with terminal isocyanate groups blocked by an alkylphenol Weight per NCO equivalent = 2400 g/eq	DESMOCAP 12	BAYER

phase, but it also depends on the ductility of the continuos phase because the mechanisms of deformation are related to the characteristics of the matrix.[5] As clearly explained by Bussi and Ishida,[6] when the elastomer co-reacts with the epoxy segments, the ductility of the system is increased as a result of the incorporation of a flexible, rubbery molecule as part of the polymer network. Similarly, Mulhaupt and Buchholz[7] refered to polymer compatibility as determining phase separation and/or flexibilization of the matrix. The use of randomly incorporating comonomers, such as telechelic liquid rubbers, can produce drastic morphological changes with respect to systems where only physical adhesion between the phases is possible.

In the present study, end-blocked urethane prepolymers (PUs) were utilized to modify an epoxy thermoset. The chemical structure of the prepolymer depended on the initial ratio of the raw materials (toluene diisocyanate and polyol). A prepolymer with a stoichiometric ratio of isocyanate to hydroxyl groups equal to unity (NCO/OH = 1) was synthesized in our laboratory (PU1) and immediately blocked with a nonylphenol for easy handling. A commercially blocked urethane prepolymer, prepared at a ratio NCO/OH = 2 (D12), was used as an alternative modifier. The epoxy–PU mixture was co-reacted (when possible) with a cycloaliphatic amine. The relation between prepolymer structure, final morphology, and final properties of the copolymers is analyzed in this work.

EXPERIMENTAL

Materials

The materials used for this study are listed in Table I. The polyol [poly(propylene oxide)glycol (PPG 1000)] and the epoxy resin (DGEBA) were heated at 80°C and deaerated under vacuum during 12 h before use. The other reactants were used as received.

Synthesis of Blocked Urethane Prepolymers (PU)

The prepolymer PU1 was synthesized in our laboratory by a two-step scheme. In the first step, PPG 1000 was reacted with toluene diisocyanate (TDI) using a ratio of NCO/OH = 1. The conditions of the reaction, selected from analysis of previous publications and preliminary tests,[8–11] were 70°C for 2 h under constant stirring and dry nitrogen atmosphere. In a second step, nonylphenol (NP) was added to the mixture to react with any terminal NCO groups, using the same reaction conditions.

According to information provided by the supplier, the commercial urethane prepolymer (D12) was synthesized from TDI and PPG using a ratio NCO/OH = 2. It should be noted that the equivalent weight of the PPG used in the synthesis of D12 is about twice the corresponding value of the PPG used for the PU1.

Epoxy–Urethane Copolymerization

The copolymers were obtained by crosslinking a DGEBA–PU mixture with a mixture of cy-

cloaliphatic amines (MA). 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.[4,9,12]

The test specimens were prepared with 0, 5, 10, 15, and 20% by weight of PU1 or D12 in the epoxy resin. DGEBA and PU were mixed at a temperature of 70°C for 30 min, deaerated, and then cooled. Finally, the amine was added, and the mixture was casted in a rectangular aluminium-Teflon mold. According to previous works, 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.[19]

Testing Methods

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to determine the molecular weight distribution of the urethane prepolymers. GPC was performed in a Waters 244 device provided with a refraction index detector. Tetrahydrofuran (THF) was used as a solvent at a 1 mL/min flow rate. Columns of Styragel of 500, 1000, 10000, and 100000 Å were used.

Differential Scanning Calorimeter

The heat evolved during the copolymerization reaction, as well as the glass transition temperatures of the final materials taken as the onset of the transition were determined using a differential scanning calorimeter (DSC; Shimadzu DSC 50) at a heating rate of 10°C/min.

Dynamic Mechanical Test

A dynamic mechanical analyzer (DMA 7, Perkin Elmer) with three-point bending geometry, was used to determine the glass transition temperatures of the copolymers as the maximum in the tan δ peak. The dimension of samples were ∼ 20 × 3 × 1 (in mm). The heating rate was 10°C/min from −70 to 180°C, and a fixed frequency of 1 Hz was used during the runs.

Bending and Compression Tests

Bending and compressive tests were performed with a Shimadzu SC 500 universal testing machine. Bending tests were run following the procedures of 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 following dimensions: bending specimens, $3 \times 12 \times 120$ mm; compression cylindrical specimens, 5×7.5 (in mm, diameter and height, respectively).

Impact Test

The impact tests were conducted with a pendulum-striker (Wolpert, PW5). Precracked test specimens were used to determine the critical strain energy release rate, G_{1C}. 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 pre-compressed specimen. G_{1C} was determined with the following equation:

$$G_{1C} = U/BW\phi \tag{1}$$

where U is the stored elastic strain energy in the specimen at the onset of crack growth, W is the width, B is the thickness of the specimen, and ϕ is a dimensionless factor that 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.[13–15] The values of U were calculated using eq. 2, which requires the direct reading of the angle of the pendulum, α, as follow:

$$U = mgl(\sin \alpha - \sin \alpha') \tag{2}$$

where m and l are the mass and the length of the pendulum, respectively, and α' is the angle measured without 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 with a profile projector (10×) to observe the surface of the broken samples. A 5-point average was used to calculate the initial crack length.

Morphology

The SEM photographs of the fracture surface of the different copolymers were taken with a scanning electron microscope Philips model SEM 505. The samples were previously coated with gold.

Micrographs were magnified, and regions containing $\sim$ 100 particles of dispersed phase were analyzed. This analysis led to the determination of the particle-size distribution, as n (number of particles) versus D (diameter) for each formulation. The average diameter of the particles and volume fraction of the dispersed phase were calculated with eqs. 3 and 4, respectively[16]:

$$D_p = \frac{\sum nD}{\sum n} \qquad (3)$$

$$V_D = (\pi/4) \sum nD^2/A_T \qquad (4)$$

where A_T is the area of the micrograph region under analysis. Equation 4 assumes that the volume fraction is an isotropic property. Hence, the values measured in the plane are the same as in the volume. In addition, the number of dispersed-phase particles by surface unity (Np) was calculated and the distances between center (d_C) and edge (d_B) of two adjacent particles were determined by direct measurement on the image.

RESULTS AND DISCUSSION

Characterization of Prepolymers

Depending on the initial ratio of the reactants (PPG and TDI), the PUs can be synthesized with different NCO reactive terminal groups. For stoichiometric conditions (NCO/OH = 1), a mono-functional prepolymer is obtained (on average, a
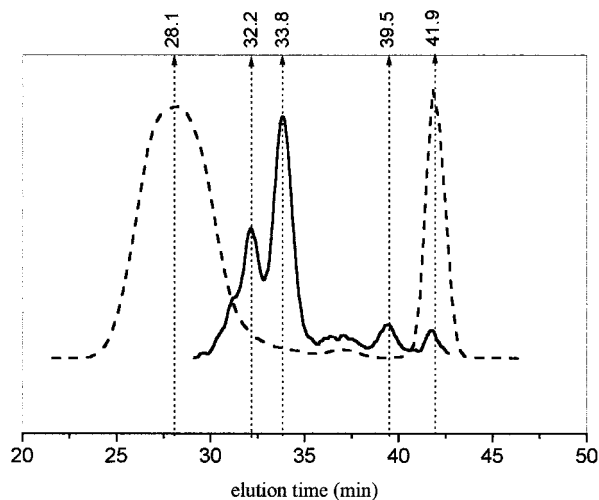
Table II   Average Molecular Weight of the Urethane Prepolymer

Prepolymer	A[a]		B[b]	
	Mn	Mw	Mn	Mw
PU1	1094	29284	16184	37720
Desmocap 12	1783	3534	3477	4023

[a] A, average values consider the complete distribution of species, including unreacted nonyl phenol.
[b] B, average values consider only the distribution of species in the polymeric part of the sample.

reactive group by each prepolymer chain). If an excess of TDI is utilized, such that NCO/OH = 2, a prepolymer with terminal NCO and average functionality equal to 2 is obtained. The gel permeation chromatography (GPC) chromatograms for PU1 and D12, indicating the elution time for each peak are shown in Figure 1. Using a polystyrene calibration, the assignment of the peaks was realized to identify the major chemical structures in the PUs. The peaks of D12 appearing at elution times of 41.9, 39.5, 33.8, and 32.2 min were assigned to the alkylphenol, blocked TDI, blocked urethane prepolymer containing one PPG chain, and blocked urethane prepolymer containing two PPG chains, respectively. The PU1 chromatogram shows the NP peak and a broad peak at an elution time of 28.1 min. This last peak corresponds to a broad distribution of large species with different number of PPG chains in their structure.

Results of the average molecular weight (Mw) determination are shown in Table II. As the NCO/OH ratio increases, the Mw decreases and its distribution is narrower. This result is expected because the excess of NCO groups limits the growing of the chains to very high molecular weight, which does not occur at the stoichiometric ratio. Thus, D12 contains mainly species with one or two PPG in their chain and a minor concentration of higher and lower molecular weight species, as can be concluded from B values in Table II or directly from the chromatograms in Figure 1. On the other hand, PU1 shows a high molecular weight and a very broad molecular weight distribution.

The glass transition temperatures (T_g) of pure PU1 and D12 were -42 and $-60°C$, respectively. The lower T_g of D12 is consequence of the higher flexibility of the chains of this prepolymer with respect to PU1, which is related to the higher

Figure 1   GPC chromatograms of PUs. (—) D12; ($\cdots$) PU1.

molecular weight of the reactive PPG used in the synthesis.

Characterization of Copolymers

The PU–amine–epoxy reactive mixtures were initially homogeneous (transparent). As the crosslinking reaction took place, a dispersed phase was segregated in the form of spherical particles. This result is due to a change in entropy originated from the increase of the molecular weight of the system.

Changes in the epoxy–amine main phase are to be expected in the case of D12 modifier because it can potentially react with the other co-monomers. On the other hand, the end blocking agent, NP, is released in the mixture during polymerization, and the amount released depends on the concentration of modifier and is higher in the case of PU1. However, work has been done on the effect of NP on the T_g and mechanical properties of an epoxy–amine sample,[19] showing that there is no measurable change even at relatively high NP concentrations.

The SEMs of the samples of PU1–epoxy–amine copolymers with 5, 10, and 15% of PU1 are shown in Figures 2a–c. The influence of the initial prepolymer concentration on the average diameter (Dp) and volume fraction of the dispersed-phase (V_D) is shown in Table III. Both morphological parameters increase with initial prepolymer concentration. In this range of PU1 concentration, the average particle size varies between 0.19 and 0.36 μm, similar to that reported in the literature for an epoxy–amine system modified with a non-reactive elastomer.[4,16] The similarity of T_gs of PU1–epoxy–amine copolymers with the pure epoxy–amine system (see Table IV) indicates that the chains of PU1 essentially do not form part of the network. Although some of them may be acting as dangling chains in the thermoset structure, they are not enough to change noticeably the T_g of the sample. This result is in agreement with the observed V_D, which is essentially equal to the volume of added rubber, ϕ_{PU}, for the 15% PU1 sample, although it is somewhat lower for the 5 and 10% PU1 samples. The V_D for PU1 samples are much closer to ϕ_{PU} than the values calculated for D12 samples.
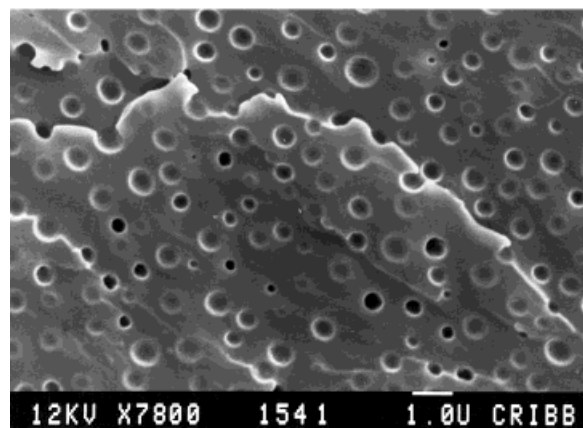
Using 20% PU1 as the modifier, a very different morphology was observed. Two different zones are shown in Figure 3 (20% PU1). In zone A, the morphology is similar to that observed at lower percentages of PU1. In this case, the size of
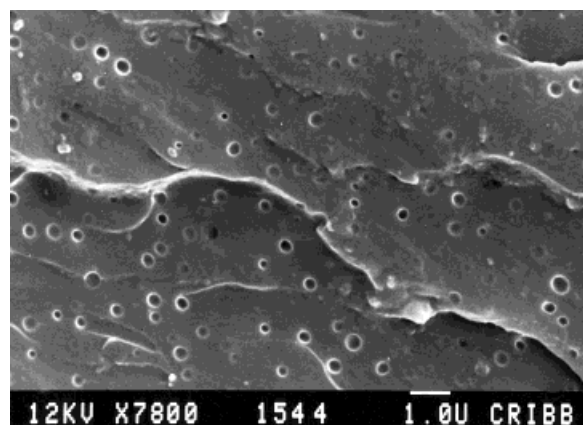
(a)
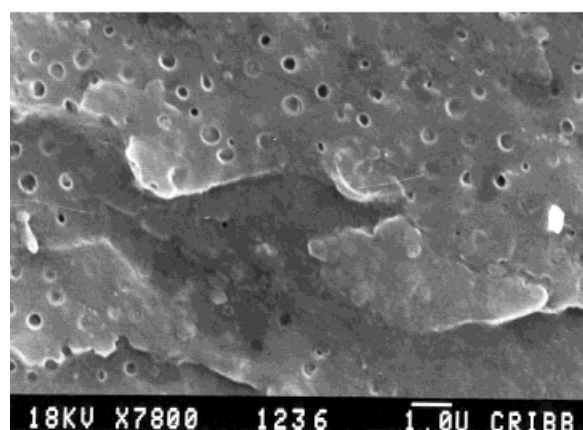
(b)

(c)

Figure 2 SEM micrographs of fractured surface of epoxy–amine (EA) copolymers with (a) 5% PU1, (b) 10% PU1, and (c) 15% PU1.

the particles is $\sim$ 0.4 μm. In Zone B, spherical nodules of $\sim$ 3–5 μm forming large agglomerates were observed. The results obtained by DMA for

Table III   Morphological Analysis of Fracture Surface of Copolymers

Prepolymer	PU1			D12	
	5%	10%	15%[c]	10%	20%
ω_{PU}[a]	0.04	0.079	0.116	0.077	0.16
ϕ_{PU}[b]	0.045	0.089	0.133	0.085	0.173
D_p (μm)	0.19	0.22	0.36	0.1	0.17
V_D	0.027	0.041	0.132	0.029	0.078
N_p (part/μm^2)	0.91	0.95	1.19	3.67	3.24
d_C (μm)	0.98	0.92	0.89	0.55	0.579
d_B (μm)	0.80	0.70	0.53	0.452	0.409
D_p/d_B	0.237	0.314	0.679	0.221	0.416

[a] Initial mass fraction of PU: mass PU/(mass epoxy + mass amine + mass PU).
[b] Initial volume fraction of PU.
[c] Initial percentage of PU: $100 \times$ mass PU/(mass epoxi + mass PU).

this particular sample show two transitions. tan δ peaks at 137°C (and 128°C by DSC) and −38°C (Figure 4) corresponding to the transition of zones A and B, respectively, were measured. The value of T_g of zone B, close to that of the pure PU1 (−42°C), indicates that this phase is very rich in the elastomer. The composition of this zone was further analyzed using chemical attack to the sample surface. Due to the low amount of chemical bonds of PU1 with the epoxy-rich phase, when the sample is attacked with an adequate solvent, zone B can be dissolved. The sample was placed in THF for 48 h, and the resulting material was observed by SEM. In Figure 5a–b, SEMs of the samples with and without attack are compared. What seems to be a co-continuos structure for this material is shown in Figure 5a. Regions A and B seem interconnected throughout the sample. After the chemical attack (Figure 5b), the region B was removed because of the action of the solvent, which left connecting voids in their place. This
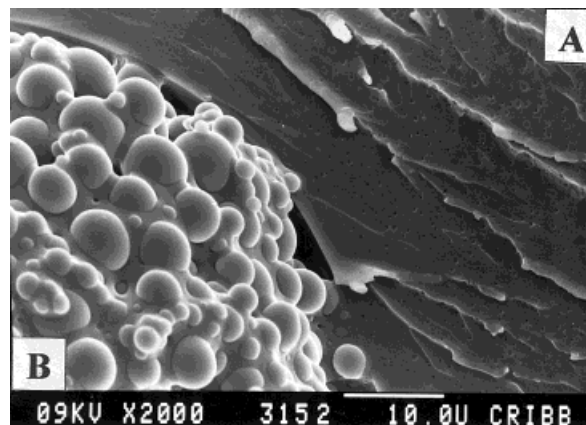

Figure 3 SEM micrographs of fractured surface of epoxy–amine (EA) copolymers with 20% PU1 in the (a) A region and (b) B region.

observation is in agreement with the statement that region B is a PU1-rich, essentially not-bonded region, and with the description of the morphology of this copolymer as a co-continuous structure.

SEMs of copolymers with 10 and 20% D12 are shown in Figures 6a and b. The D_p and V_D increase with the initial concentration of prepolymer (Table III). The average particle size (0.1–0.17 μm) is smaller than the D_p measured in PU1-modified samples because of the larger concentration of the reactive end groups. The size and concentration of disperse phase indicate that a large amount of D12 is co-reacted in the continuous phase, contrary to the observations for the copolymers of PU1. The T_gs of the copolymers decrease with the amount of modifier (130, 124, and 118°C corresponding to 0, 10, and 20% D12, respectively), as shown in Table IV. In this system, the chains of D12 have a higher probability of co-reaction with the epoxy–amine system than PU1 and, therefore, the thermoset is flexibilized.

In addition to the observed effect of the reactivity of the PU modifiers (D12 systems show a

Table IV   Mechanical and Thermal Properties of Copolymers

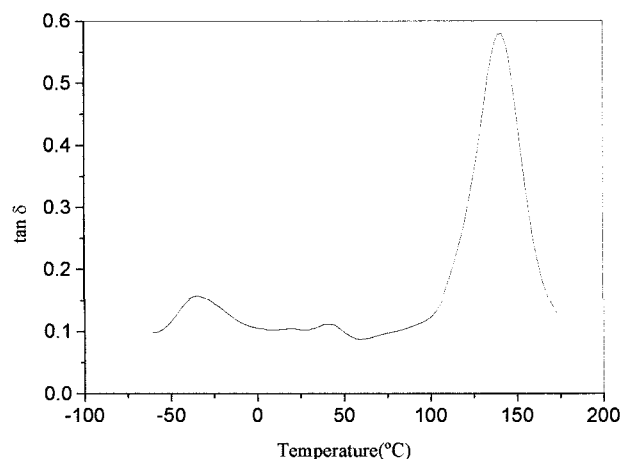| Sample	E_F (Gpa)	σ_{CY} (Mpa)	G_{IC} (kJ/m^2)	T_g (°C)
Epoxy–amine (EA)	2.80 ± 0.17	113 ± 7	0.456 ± 0.062	130 ± 2
EA–PU1 (5%)	2.70 ± 0.3	112 ± 1	0.582 ± 0.056	133 ± 2
EA–PU1 (10%)	2.30 ± 0.5	105 ± 2	0.584 ± 0.04	128 ± 2
EA–PU1 (15%)	2.17 ± 0.16	102 ± 4	0.715 ± 0.06	126 ± 2
EA–PU1 (20%)	1.48 ± 0.2	46 ± 3	1.677 ± 0.152	128 ± 2
EA–D12 (10%)	2.60 ± 0.1	105 ± 3	0.646 ± 0.032	124 ± 2
EA–D12 (20%)	1.99 ± 0.15	89 ± 4	0.771 ± 0.062	118 ± 2

**Figure 4** Curve of tan δ–temperature for epoxy–amine with 20% PU1.

main T_g decreasing with rubber concentration), the molecular weight of the PUs also has an important effect on phase separation. Thus, the unreactive and high molecular weight PU1 leads to a phase-separated system with larger rubber domains at low concentrations, and the system reaches the critical concentration for bicontinuous structures to appear at lower rubber contents than the D12 system.

Mechanical and Fracture Properties of Copolymers

The dependence of flexural modulus (E_F) and compression yield stress (σ_{YC}) of the copolymers on the initial mass fraction of prepolymer (ω_{PU}) is shown in Table IV. In all cases, E_F and σ_{CY} decrease with the content of prepolymer. There are two factors causing the drop of the modulus: the increase of the volume fraction of elastomeric dispersed phase (the rigid phase decreases) and the decrease of rigidity of the continuous phase due to the copolymerization with the prepolymer. Regarding the last effect, Wang and Chen[17] worked with a similar system and reported that the modulus of the network at room temperature decreases due to the effect of the soft segment structure of the co-reacted elastomer. Because PU1 is practically not co-reacted to the continuous phase, the decrease in the modulus can only be explained to be due to the increment of the V_D and, consequently, the decrement of the rigid continuous phase. A steep drop in the modulus was observed at 20% PU1 due to the particular co-continuous morphology observed at this percentage. When D12 was used as modifier, the increase of the dispersed phase as well as the modification

of continuous phase should contribute to the modulus reduction. In this case, as the initial fraction of prepolymer increases, the continuous phase is "flexibilized" due to the copolymerization with the soft chains of prepolymer. In other words, as the initial amount of elastomer increases, a different and more flexible continuous phase is generated.

The values of compressive yield stress of the samples modified up to 15% PU1 decrease slightly as the percentage of elastomer increase. On the contrary, the compressive yield stress for the sample with 20% PU1 decreases greatly due to the effect of its particular co-continuous morphology. The compressive yield stress of the samples modified with D12 show a similar trend as the percent D12 increases, but the decrease is less steep because the morphology is that of spherical rubber inclusions, even at 20% D12.
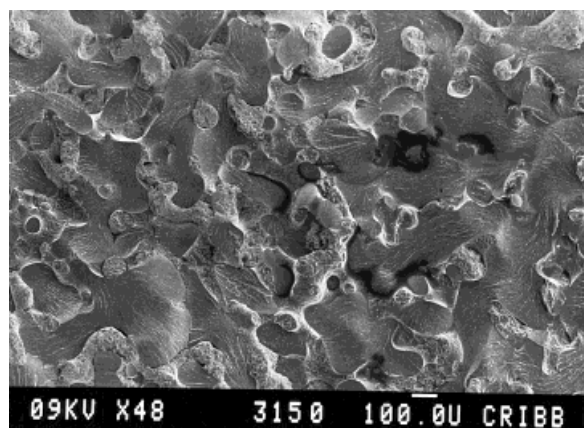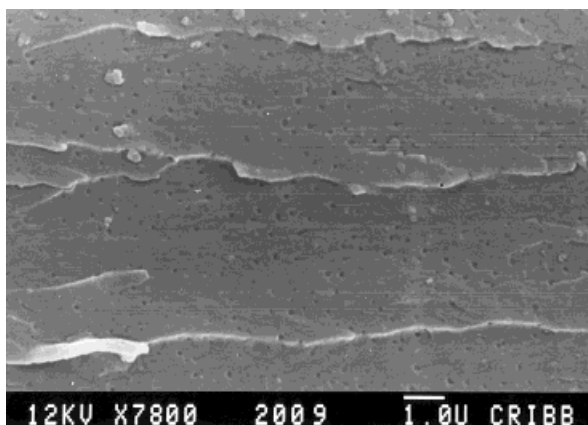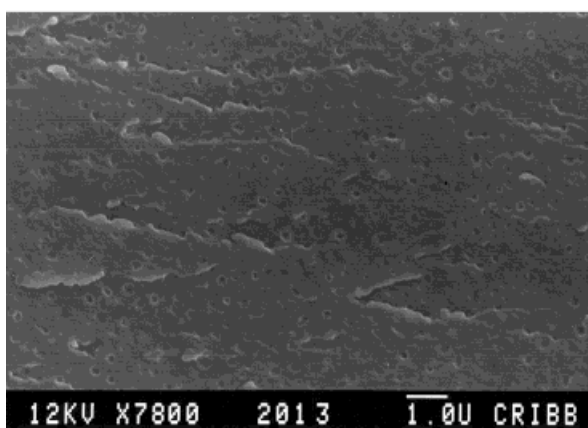

(a)
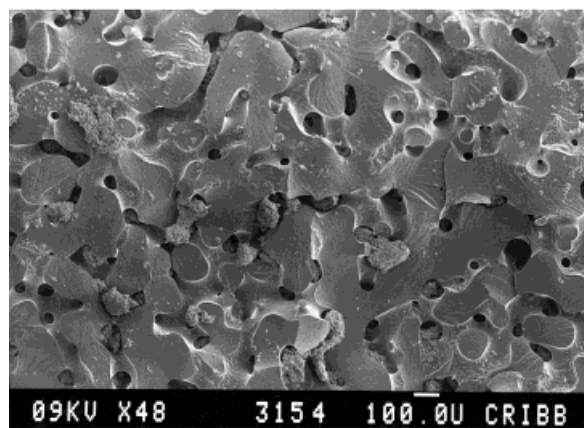
(b)

Figure 5 SEM micrographs of fractured surface of epoxy–amine (EA) copolymers with 20% PU1: (a) sample without attack; (b) sample attacked with solvent.

(a)

(b)

Figure 6 SEM micrographs of fractured surface of epoxy-amine (EA) copolymers with (a) 10% D12 and (b) 20% D12.

The values of G_{IC} for the copolymers are shown in Table IV. In all cases, G_{IC} increases as the initial concentration of prepolymer increases. It has been frequently reported in the literature that the elastomer particles promote the multiple, but localized, shear-yielding in the matrix initiated by the stress concentrations associated with the presence of the rubbery particles. However, G_{IC} increases only very slowly with increasing volume fractions of dispersed phase at high testing rate. This effect can be explained as a consequence of the reduced shear deformation as testing rate increases, according to previous works.[1,20]

For the same value of V_D, the samples modified with D12 present a larger value of G_{IC} (i.e., 5% PU1 and 10% D12). However, they also show a larger number of particles of smaller size. The smaller size of the particles of dispersed phase

has been previously reported as the cause of improved toughening.[3] The ductility of the matrix also has an important effect on the fracture energy of the material.[5] When the system is modified with D12, the ductility of the network increases due to the copolymerization of the epoxy–amine with the flexible PUs chains and, thus, the presence of the rubber particles is more effective in toughening the thermoset. In the case of the 20% PU1 sample, there is a large increment of G_{IC}. The particular co-continuous structure observed by SEM is the cause of this increase in the measured fracture energy and the much reduced mechanical properties of this sample.

CONCLUSIONS

The modification of epoxy resins with urethane prepolymers produced an improvement in the toughness with respect to the net epoxy–amine system. The final copolymer characteristics depend on the structure of the prepolymer used as modifier. When PU1 was used as modifier (up to 15% PU1), the co-reaction with the epoxy resins practically does not occur because of the low concentration of end NCO groups. The similar T_g of the modified system with respect to pure epoxy confirms this result. On the other hand, by using D12 as modifier, the network thermoset was ductilized because of the copolymerization with flexible chains of prepolymer. In this last case, the T_gs of copolymers decrease as the concentration of prepolymer increases. This result was also confirmed by the low volume of the separated rubber phase in the case of D12 samples.

The average size (D_p) and volume fraction (V_D) of dispersed second phase increased with initial concentration of prepolymer. Also, for a given initial concentration of prepolymer, V_D and D_p decrease as the end NCO groups of prepolymer increase, in agreement with the lower T_g measured for the modified system with D12. The G_{IC} values show a moderate increase as V_D increase as was expected for the high rate test, but the mechanical properties slightly decrease.

By using 20% PU1, an unreactive and high molecular weight modifier, a critical concentration region of epoxy mixture–rubber is reached, for which a co-continuous morphology is observed in the final thermoset. This morphology produces a large improvement in the toughness of final thermoset, but is accompanied by a large drop of mechanical properties.

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