Thermoplastic-Modified Epoxy Resins Cured with Different Functionalities Amine Mixtures: Morphology, Thermal Behavior, and Mechanical Properties

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ABSTRACT: Epoxy matrices inherent brittleness and poor crack resistance make necessary some form of toughening. In this work, to improve their fracture toughness and ductility epoxy matrices were modified by changing its architecture and by the addition of a third component. The matrices architecture were modified by stoichiometrically reacting a bifunctional epoxy resin with different functionalities amine mixtures, one of which being a monoamine that plays the role of chain extender. In the modification by the addition of a third component, poly(methyl methacrylate) (PMMA) was selected as modifier. PMMA is initially miscible with epoxy/amine systems but can phase separate during curing. The kinetics and miscibility of these systems were studied previously. At constant curing conditions, materials from completely opaque (phase separated) to transparent (miscible) can be obtained with the increase in monoamine content. In this work, the effects of the modifier content and of the monoamine : diamine ratio in stoichiometric epoxy/amine mixtures on the resultant morphologies as well as on their thermal and mechanical properties was studied.© 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1753–1760, 2009

Key words: thermosets; reaction-induced phase separation; functionality; mechanical properties; structure-property relations

INTRODUCTION

Epoxy resins present excellent performance properties, high strength and stiffness, good dielectric behavior, resistance to chemicals and corrosion, low shrinkage during cure, and good thermal characteristics.[1] However, they are brittle because of their high-crosslink density.[2] Fracture toughness can be enhanced by the incorporation of initially miscible thermoplastics, which phase separate during curing of epoxy matrices.[1,3–13] Recently, modified thermoset systems are also receiving increasing attention for special applications, where transparency is desired.[14–16] The final transparent material can present an improvement in fracture toughness without loss of the mechanical properties when hydrogen bonding interactions are present.[14]

On the other hand, modification of the epoxy matrix structure is also an effective method to improve fracture toughness.[17–39] The change in the matrices crosslink density, by modifying the initial epoxy/amine stoichiometric ratio,[23–27] by stopping the reaction at different conversion values, or by varying the curing cycles[23–26,28–29] can be suitable methods, but networks generated in this way possess lateral chains and soluble fractions, which could induce a plasticization effect. It is also possible to tailor and improve matrices properties for specific applications, choosing between the wide variety of available curing agents and epoxy resins. The chemical structure and functionality of the reactants control the development and the crosslink density of the network. In this way, the increase of the molecular mass of epoxy or amine monomers[17–22] can easily modify the architecture of the final matrix, but a wide distribution of the molecular mass between crosslink points is obtained, being generated more heterogeneous matrices. The chemical modification from a given

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rigid epoxy backbone to a more flexible backbone structure[38] also modify the final properties but the change in the network flexibility superimposes that in the molecular mass between crosslinks. Another method to achieve this modification is by reacting a bifunctional epoxy resin with a mixture of amines of different functionalities, one of which being a monoamine that plays the role of a chain extender.[17–19,30–37,39–41] In this way, full reacted networks are obtained without lateral chains and secondary reactions are avoided working at epoxy/amine stoichiometric ratio. Selecting amines with a similar chemical structure, the change in the system composition is minimum avoiding the variation in chain flexibility between crosslink points.

In this work, to improve both fracture toughness and ductility of epoxy matrices, they were modified by the addition of a third component and by modifying the architecture of the matrices. In this way, it is possible to approximate the behavior of industrial epoxy/amine formulations, which are often composed of a mixture of some modifiers, epoxy, and amine molecules, which can have different functionalities making more difficult the analysis. A diamine and a monoamine with identical chemical structure were chosen. With the couple of amines selected not only the reactivity but also the miscibility of the systems changes. At certain curing conditions, diamine can cause modifier phase separation, whereas monoamine favors its miscibility. The influence of the modifier content and of the different monoamine : diamine ratio on the resultant morphologies, thermal and mechanical properties of stoichiometric epoxy/amine formulations was analyzed.

EXPERIMENTAL

The epoxy monomer used in this study was DER332, a difunctional diglycidyl ether of bisphenol A (DGEBA), supplied by Dow Chemical. It has an equivalent mass of around 175 g/eq and a hydroxyl/epoxy ratio of 0.015. The curing agent was 4,4′-diaminodiphenylmethane (DDM), Ciba-Geigy HT972, a solid difunctional aromatic amine with a molecular mass of 198 g/mol. A solid monofunctional aromatic primary amine, *p*-toluidine, Fluka, with a molecular mass of 107 g/mol, was used as a chain extender. Poly(methyl methacrylate) (PMMA), Aldrich 200336, was used as modifier. It had a mass average molecular mass, M_w, of 15,200 g/mol and a polydispersity index of 2.1 referred to polystyrene standards, as measured using a Perking-Elmer LC-295 gel permeation chromatograph, equipped with three Waters Styragel columns HR2, HR4 and HR5E, employing tetrahydrofurane (THF) as eluent. DGEBA and PMMA were placed in a vacuum oven at 80°C overnight to remove any water present and amines were used as received without purification. Both amines have a similar chemical structure to ensure similar composition of the resultant products.

The corresponding amounts of PMMA were dissolved in dichloromethane, and the resin was added with mechanical stirring. The solution was placed in an oil bath at 90°C for several hours and thereafter, held overnight under vacuum at 90°C. At this point, no phase separation was observed by differential scanning calorimetry (DSC) over the range 30–200°C. Then, *p*-toluidine : DDM mixtures were added at 80°C stirring vigorously for 5 min. Stoichiometric epoxy/amine equivalent ratio was used. Mixtures of amines were carried out at the following ratios of monoamine : diamine equivalents: 0 : 100, 25 : 75, 50 : 50, 75 : 25, and 100 : 0. PMMA contents in these matrices were 15, 20, 30, and 40 wt %. The corresponding neat matrices were also prepared by the same procedure. All mixtures were poured into preheated molds at 130°C and cured 5.5 h at this temperature using vacuum during the first stages. The high precure temperature was used to ensure PMMA phase separation in DGEBA/DDM system.[42] Finally, they were postcured 2 h at 190°C. Specimens were mechanized for the dimensions required for the different analysis.

Morphologies of cryogenically fractured surfaces were analyzed by atomic force microscopy (AFM). AFM scanning was performed at room temperature with a scanning probe microscope Nanoscope IIIa Multimode from Digital Instruments operating in tapping mode using a tip with 5–10 nm of curvature nominal radius. Several regions were scanned obtaining similar images. Phase images are presented. One ultramicrotomed sample was also analyzed by transmission electron microscopy (TEM) by using a Hitachi 7000FA microscope, operating at 100 kV accelerating voltage. Ultrathin section was stained with ruthenium tetroxide (RuO_4) vapors for 1 h to enhance contrast between phases.

Dynamic-mechanical analysis (DMA) was carried out in a Perkin-Elmer DMA-7 analyzer using a three-point bending device. DMA measurements were carried out with $24 \times 3 \times 2$ mm^3 specimens maintaining a span of 10 mm and using 90 and 80 mN as static and dynamic forces, respectively. All measurements were carried out at a constant frequency of 1 Hz with a heating rate of 5°C/min using helium atmosphere.

Flexural properties were determined in a three-point bending device using a Instron universal testing machine, model 4026, equipped with a load cell of 1 kN. Tests were carried out at room temperature with a relative humidity of 50 ± 5% using a crosshead displacement rate of 2.1 mm/min. The $100 \times 10 \times 5$ mm^3 specimens were analyzed with a

TABLE I
T_g Values of the Different PMMA Modified Epoxy Matrices

	p-toluidine : DDM ratio									
	0 : 100		25 : 75		50 : 50		75 : 25		100 : 0	
PMMA (wt %)	Epoxy rich	PMMA rich	Epoxy rich	PMMA rich	Epoxy rich	PMMA rich	Epoxy rich	PMMA rich	Epoxy rich	PMMA rich
0	195.5		165.0	–	143.5	–	126.5	–	105.5	–
15	177.0	142.0	144.5	116.0	119.5		104.0	–	100.5	–
20	185.0	119.0	138.5	106.5	112.0		107.0	–	102.0	–
30	184.0	116.5	139.0	102.5	112.0	77.0	104.5	–	99.5	–
40	178.0	116.0	145.5	103.0	119.0	78.0	108.5	–	101.5	–

span of 80 mm in accordance to ASTM D-790-93 standard.

Fracture toughness measurements were analyzed for determining the critical stress intensity factor (K_{IC}) in a Instron universal testing machine, model 4026, equipped with a three-point bending device. $60 \times 12 \times 5$ mm^3 specimens were notched with a saw and a precrack was initiated at the roof of the notch with a razor blade. The notch and crack dimensions were determined by optical microscopy. Tests were carried out at room temperature with a relative humidity of $50 \pm 5\%$ using a crosshead displacement rate of 1.7 mm/min and a span of 48 mm in accordance to ASTM D-5045-91. Results were the average of at least 5 measurements.

RESULTS AND DISCUSSION

As previously demonstrated,[40,41] the employment of the selected couple of amines in preestablished concentrations is a reliable method to modify the network architecture from a highly crosslinked network to a linear polymer. Glass transition temperature (T_g) of these matrices decreased with monoamine content because of its plasticization effect.[40] T_g values of the neat matrices measured by DMA are reported in Table I along with T_g values of modified systems discussed later. Mechanical properties of neat matrices tested showing that modification of the network architecture by introducing an increasing amount of chain extender in the aminic hardener formulation is a reliable method to improve fracture toughness, as it was also shown elsewhere.[41] Mechanical properties of neat and modified systems are collected in Figures 1–3. First, the influence of chain extender is discussed. Values of both elastic modulus (E) and maximum strength (σ_{max}) increased as chain extender content was higher due to the lower local mobility at room temperature. With except to the systems cured with both di- and monoamine, all the others yielded before breakage. The chain extender introduction in the aminic formulation increases intermolecular interactions thus diminishing the secondary β relaxation corresponding to short-range cooperative motions involving —CH_2–CH(OH)—CH_2–O— units in both temperature and strength.[41] The lower flexural strength and fracture toughness for the linear polymer obtained by

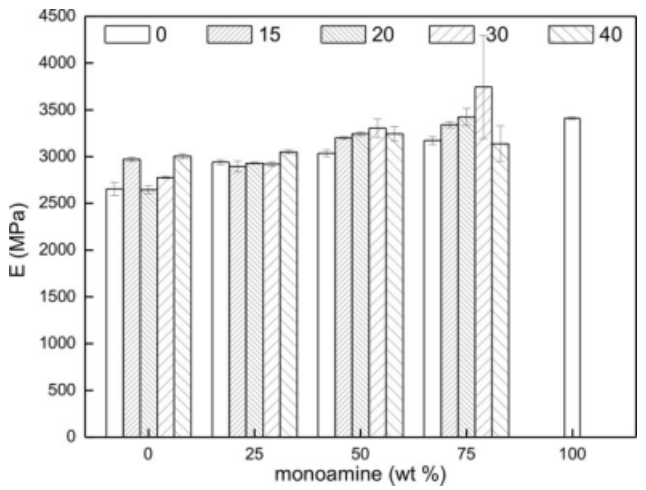


Figure 1 Flexural elastic modulus for DGEBA/amine mixtures containing several *p*-toluidine : DDM ratios, neat and modified with PMMA.

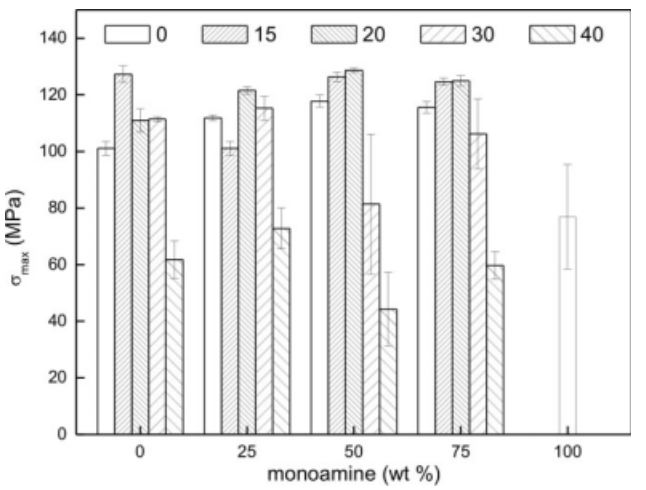


Figure 2 Flexural strength for DGEBA/amine mixtures containing several *p*-toluidine : DDM ratios, neat and modified with PMMA.

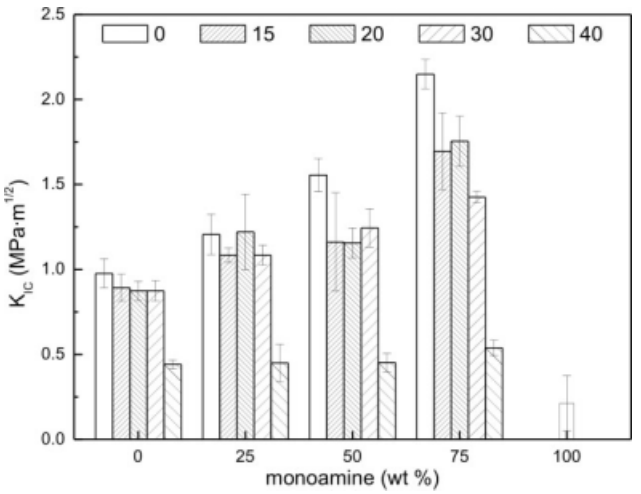


Figure 3 Critical stress intensity factor for DGEBA/amine mixtures containing several *p*-toluidine : DDM ratios, neat and modified with PMMA.

reacting the epoxy resin with the monoamine is surely linked to the low molecular weight in the linear DGEBA/monoamine mixture due to the practical impossibility for achieving very high conversion on this system.

These epoxy/amine mixtures were modified with PMMA. PMMA is initially miscible with epoxy precursors but can phase separate during curing. The resultant morphologies were analyzed by AFM. It is interesting to note that with selected couple of amines, the miscibility of PMMA in the systems changes.[43] The reaction of *p*-toluidine with DGEBA does not induce phase separation of PMMA. However, reaction of DGEBA with DDM can induce phase separation at conversions near system gelation[42] depending on modifier content and curing conditions. This fact is due to variation on the entropic contribution for higher crosslinked networks. Apparently, monoamine acts as a compatibilizer of PMMA in mixtures cured with DDM, as can be corroborated from final appearance of 5 mm thick samples of these systems cured at 130°C, shown in Table II. Opaque materials result for PMMA-modified DGEBA/DDM system, whereas completely transparent materials are obtained for the system reacted with monoamine. In blends formed by a mixture of both amines, the occurrence of PMMA phase separation depends on mono : diamine ratio in the mixture as well. The addition of monoamine delays to higher epoxy group conversions the phase separation process (when it occurs) until average conversion values close to gelation conversions of each system, calculated from Flory–Stockmayer theory. Besides the enthalpic contribution due to the change in the chemistry of the system during reaction, the entropic contribution to the free energy seems to be the main responsible for the differences found in the conversions associated to phase separation for the different mixtures. The modification of phase separation conversions can also allow tuning the size of PMMA domains.[44]

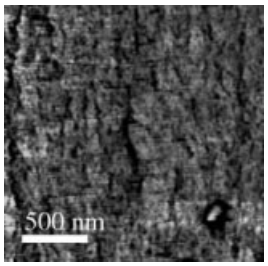
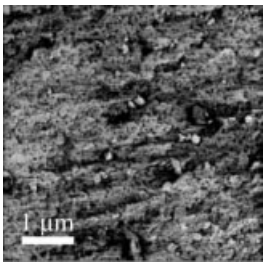
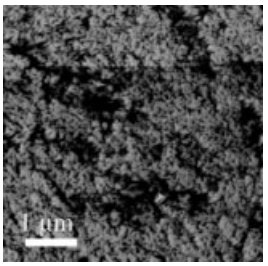
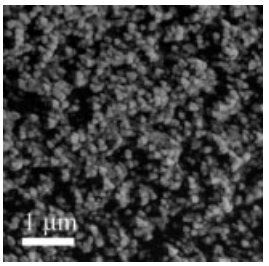
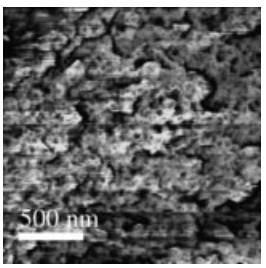
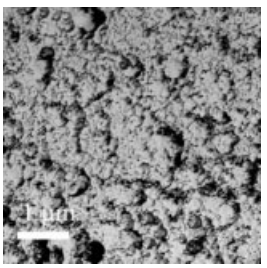
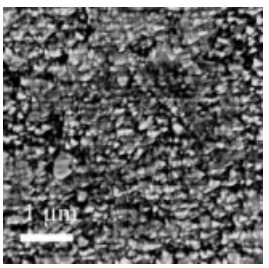
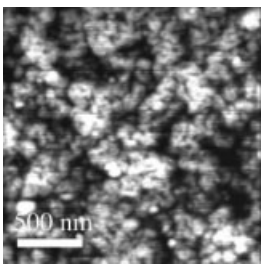
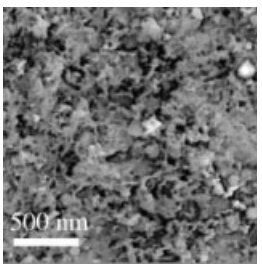
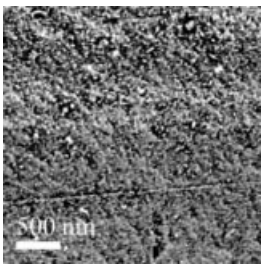
Table III shows AFM phase images corresponding to different systems. The high proximity of phase separation and gelation of matrices seems to stop phase separation in early stages, thus materials with low-size domains are obtained. In the system with the highest DDM content, the modification with 15 wt % PMMA leads to a particulated morphology with nanodomains dispersed in an epoxy-rich matrix. The obtained domains show a broad range of sizes, between 10 and 65 nm. This morphology was corroborated by TEM, as shown in Figure 4. In the system modified with 20 wt % PMMA, the number and size of the domains increases obtaining particles between 40 and 85 nm. As a result of the thickness of these 15 and 20 wt % PMMA-modified epoxy particulated materials, a final cloudy or opaque appearance is obtained due to the fact that the light has to pass through a great number of planes. Particles manage to scatter the light. The PMMA miscibility in the matrix increases with the amount of monoamine in the system, and therefore miscible materials or particulated systems with lower size domains are obtained as in the case of the mixture with *p*-toluidine : DDM ratio 25 : 75 with a 20 wt % PMMA, whose AFM image shows domains between 20 and 60 nm. Higher monoamine contents in the aminic hardener formulation lead to miscible systems.

Increasing the presence of PMMA in the system, mixtures present very different morphologies. DGEBA/DDM system modified with 30 wt % PMMA shows a cocontinuous morphology similar to that found by other authors for the same matrix modified with a higher molecular mass PMMA at lower curing temperatures.[11,45,46] When the monoamine content increases, cocontinuous structures are also obtained until a miscible mixture is observed when a monoamine : diamine ratio 75 : 25 is

TABLE II
Final Appearance of 5 mm Thick Samples for the Different PMMA Modified Matrices

p-toluidine : DDM	PMMA (wt %)			
	15	20	30	40
0 : 100				
25 : 75				
50 : 50				
75 : 25				
100 : 0				

TABLE III
AFM images for the Different PMMA Modified Epoxy Matrices

	PMMA (wt %)			
p-toluidine : DDM	15	20	30	40
0 : 100				
25 : 75				
50 : 50				
75 : 25				

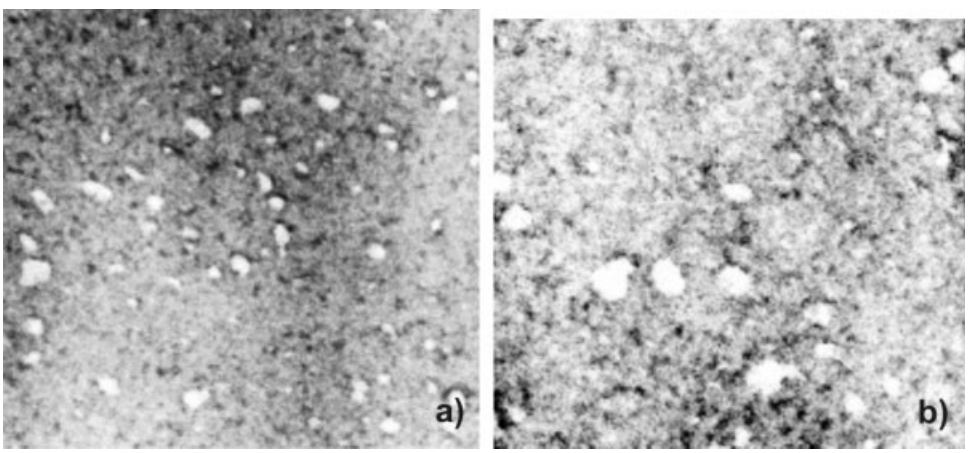


Figure 4 TEM micrographs for DGEBA/DDM mixture modified with 15 wt % PMMA. (a) ×40,000 and (b) ×80,000.

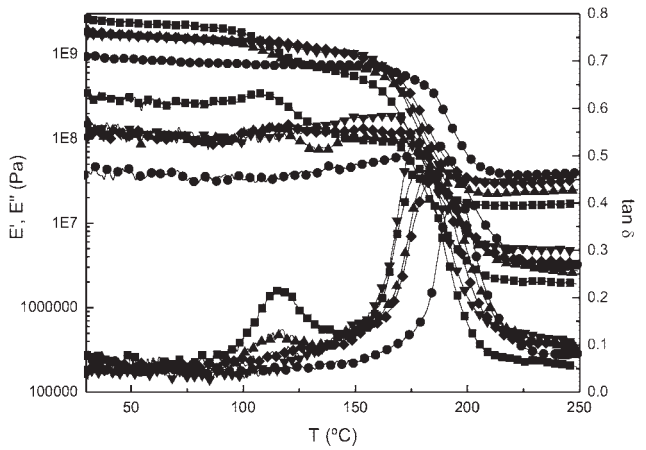


Figure 5 Dynamic-mechanical behavior for DGEBA/DDM mixtures, (●) neat and modified with: (▼) 15, (◆) 20, (▲) 30, and (■) 40 wt % PMMA.

employed. In DGEBA/DDM system with 40 wt % modifier, the morphology completely changes, but it remains being cocontinuous. A specimen of this system maintained for 24 h at reflux in dichloromethane showed swelling but not its disintegration. DMA measurements and mechanical tests also indicated that epoxy-rich phase was the matrix of the system, as discussed later in the text.

Increasing the monoamine content in the aminic hardener formulation, more irregular structures are formed. As phase separation is delayed to higher conversion on increasing of monoamine content,[43] the domain size and shape change as a consequence of this increased miscibility between components that even results in completely transparent mixture in the case of neat monoamine.

To obtain more information about the composition of generated phases, mixtures were also analyzed by DMA. Figure 5 shows the storage modulus (E'), loss modulus (E'') and loss factor (tan δ) for blends of DGEBA/DDM modified with 0–40 wt % PMMA. The T_g of PMMA, measured by DMA, is about 110°C. In modified systems, α relaxation associated to the thermoset-rich phase is shifted to temperatures lower than the corresponding to the neat matrix. However, E'' curve points out the presence of phase separated PMMA in all of them. In 15 wt % PMMA-modified system, a wide shoulder appears between the α relaxation assigned to epoxy-rich phase and the region where PMMA transition is observed. A fall in E' curve previous to that of the matrix relaxation is also observed. The position of this relaxation, collected in Table I, indicates that PMMA contains a high amount of highly reacted epoxy/amine segments. In systems with higher modifier contents, PMMA α relaxation is clearer. Its position is also shifted respect to the value of neat PMMA, giving advice that possibly unstoichiometric epoxy/amine chains remain in the PMMA-rich phase, thus leading to the existence of a lower epoxy/amine stoichiometric ratio in the epoxy-rich phase. The decrease in epoxy-rich phase T_g value, also shown in Table I, is ascribed to some amount of PMMA remained dissolved. The existence of a lower epoxy/amine stoichiometric ratio in the epoxy-rich phase can also contribute to the lower T_g values.

The increase in monoamine content caused the reduction of the thermoset α relaxation temperature. In blends with *p*-toluidine : DDM 25 : 75 ratio, shown in Figure 6, the modification with PMMA caused a shift to lower temperatures of the α relaxation associated with the thermoset-rich phase, also ascribed to the remaining PMMA dissolved in the matrix and to the possible stoichiometric imbalance after phase separation. In 15 wt % PMMA-modified system, although a clear morphology was not evident from AFM, E'' curve seems to present a slight shoulder, which could correspond to a low amount of a PMMA-rich phase separated into crosslinked epoxy matrix. The phase separation could were stopped in the first stages of the process (although not shown, mixtures with higher contents of monoamine modified with 15 wt % PMMA remained miscible after curing). The relaxation assigned to PMMA increases in intensity with the modifier content. Its position is slightly different than that of pure PMMA, thus indicating the presence of epoxy/amine oligomer in this phase. The intensity of PMMA relaxation and the fall in E', lower than the observed for DGEBA/DDM modified systems, indicate the presence of a lower amount of phase separated PMMA, corroborating the higher miscibility of PMMA in matrices with higher monoamine contents. In modified epoxy/amine mixtures containing *p*-toluidine : DDM 50 : 50 and 75 : 25 ratios,

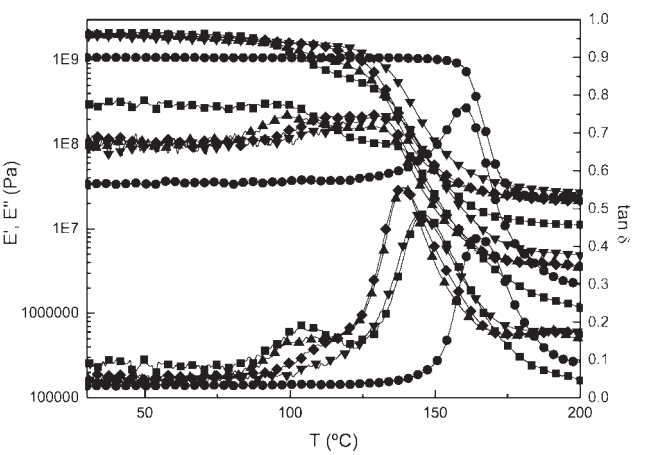


Figure 6 Dynamic-mechanical behavior for DGEBA/amine mixtures containing *p*-toluidine : DDM ratio 25 : 75, (●) neat and modified with: (▼) 15, (◆) 20, (▲) 30, and (■) 40 wt % PMMA.

although not shown, the higher miscibility of PMMA in these matrices and the possible stoichiometric imbalance after PMMA phase separation shifted their main relaxations to temperatures in the range of PMMA. However, the position of thermoset-rich phase, collected in Table I, seems to point out that in systems with 50 : 50 ratio modified with 30 and 40 wt % PMMA two phases were present, as a shift of this relaxation to higher temperatures was observed. In the same way, in the system with the ratio 75 : 25, the sample modified with 40 wt % PMMA was cloudy and its major relaxation appeared at slightly higher temperatures with respect to that modified with lower PMMA contents.

Specimens of epoxy/amine mixtures that possess diamine in the formulation kept its rigidity once T_g was overcome with a plateau in the storage modulus in the rubber region (E_r'). Indeed, the matrix was made up of the thermoset-rich phase. E_r' value diminished with PMMA content as a result of the high amount of modifier that remained dissolved in the matrix.

In DGEBA/*p*-toluidine systems, PMMA remained miscible in the whole composition range. The main T_g of modified samples was slightly lower, which can be due to the dispersion of the results. For linear systems, the elastic modulus does not recover once overcome the blend's T_g.

Mechanical properties of the different modified matrices were also analyzed. Values for flexural modulus are represented in Figure 1. PMMA addition did not lead to significant variations in E values, as both PMMA and epoxy are glassy at room temperature. In case of the modified linear polymer, its fragility prevented for mechanizing specimens with the required dimensions to carry out mechanical tests.

Flexural strength and fracture toughness values are shown in Figures 2 and 3, respectively. No significant improvements were observed because of thermoplastic addition. The addition of 40 wt % PMMA resulted in a very brittle material fracture occurring long before yielding. σ_{max} and K_{IC} values for PMMA are expected to be low because of its low molecular mass.[47]

CONCLUSIONS

The modification of epoxy matrices architecture by the use of an epoxy resin reacted with a mixture of amines of different functionalities, one of which being a monoamine that plays the role of chain extender, is an effective method to improve their mechanical properties. The increase in the monoamine content of the mixture leads to an improvement in flexural modulus, strength, and fracture toughness. Nevertheless, the modification of the different matrices with PMMA did not lead to a significant improvement of mechanical properties. The effect of crosslink density is more significant for the improvement of mechanical properties than the effect of thermoplastic addition.

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