Chemorheology and Ultimate Behavior of Epoxy-Amine Mixtures Modified with a Liquid Oligomer

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ABSTRACT: Rubber toughening of epoxy resins has been actively studied since the 1960s with clear progress in understanding of the ultimate properties: microstructure relationships. The morphology, obtained after curing of the modified thermosetting matrix, is a function of the process conditions as well as of the materials used because both influence the thermodynamics and the kinetics of phase separation. In this work several amounts of poly(oxypropylentriamine) (POPTA), have been added as modifier to a diglycidyl ether of bisphenol-A (DGEBA)-based epoxy matrix cured with a cycloaliphatic amine. Molecular weight of the neat resin and amine/epoxy stoichiometric ratio have also been used as variables. This investigation has focused upon the importance of cure chemorheology for microstructure formation by using both physicochemical (isothermal and dynamic calorimetry) and rheological techniques. In the second part of this study, the influence of the molecular weight of the epoxy resin in the ultimate properties of 15 wt % POPTA-modified epoxy matrices is also analyzed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1269–1279, 2000

Key words: epoxy-amine/oligomer; rheokinetics; morphology; ultimate properties

INTRODUCTION

The desirable properties such as high modulus, creep resistance, and good elevated temperature properties of cured epoxy resins have as counterpart that the unmodified matrices are often brittle and show poor resistance to crack propagation. Rubbery modification of epoxy resins has been extensively investigated in the latter years[1–10] because of its potential to toughen thermosetting matrices. A modifier-rich phase segregated from the matrix through curing can allow to change the mechanism of crack propagation and, conse-quently, to improve the fracture toughness of thermosetting matrices.

In this process, the modifier has to be initially miscible with the resin and curing agent. Through resin polymerization, the size increase of the oligomeric species, and therefore the corresponding decrease in the entropic contribution to the free energy of mixing, causes a modifier-rich phase to segregate from the matrix at a particular conversion level. As polymerization proceeds there is an increase in the concentration and size of the dispersed-phase particles. When the matrix gelates, this primary phase separation is practically finished, but a secondary phase separation may continue inside the dispersed-phase particles. The relative concentration of both monomers in the segregated phase may differ from that in

the initial formulation because of selective segregation. This leads to a departure from stoichiometry for both phases and can lead to important variations in the kinetics and rheology of curing for the modified mixtures with respect to that for the neat ones,[11–15] so that the study of chemorheology of polymerization and phase separation behavior becomes completely necessary in order to understand the final morphologies generated, and hence, their influence in the ultimate properties of the modified matrices. In this way, a first objective of the present study was to analyze the cure chemorheology of epoxy matrices modified with a liquid elastomer as poly(oxypropylentriamine) (POPTA).

Some researchers have examined the effect of cross-link density on the mechanical properties of modified and unmodified epoxy matrices.[4,6,16–25] Although other physical parameters can influence the ultimate properties, both cross-link density and chemical structure of the epoxy matrix are the key variables to control in order to understand the fracture behavior of these materials.

We have previously shown that liquid oligomers as POPTA can be fruitfully used for toughness improving on epoxy matrices,[25–27] also reporting the influence of the cross-link density of the network as a function of amine/epoxy ratio in the fracture properties of these mixtures. The second objective of the current investigation was to establish comparatively the efficacy of POPTA oligomer for toughening epoxy matrices with different cross-link densities obtained by using epoxy oligomers with several molecular weights.

EXPERIMENTAL

The epoxy resin used in this work for chemorheological analysis was DER-332, a diglycidyl ether of bisphenol-A (DGEBA), kindly supplied by Dow Chemical, having an epoxy equivalent (EE) weight of around 175 and a hydroxyl/epoxy ratio close to 0.03. The glass transition temperature, T_g, was −13°C, as measured by differential scanning calorimetry (DSC). A homologous series of DGEBA resins with several molecular weights, Rutapox series, gifted by Bakelite Iberica, was also used to investigate the influence of the molecular weight of the resin in the ultimate properties of the materials studied. The epoxy equivalent weights of these resins are shown in Table I. The curing agent was BASF Laromin C-260, 4,4′-diamino-3,3′-dimethyl dicyclohexyl methane, des-

Table I Epoxy Equivalent Weights for the Several Epoxy Resins Used

Epoxy Resin	Epoxy Equivalent
DER-332	175
Rutapox-0162	173
Rutapox-0164	188
Rutapox-0165	208
Rutapox-0180	375

ignated 3DCM in this paper. The functionalized elastomer, POPTA, was a liquid Jeffamine T-5000, kindly provided by Huntsman. It has a molar mass of around 5000 and $T_g \approx -66°C$ as measured by DSC, taking its value as the inflection point in the glass region.

Mixtures were made by dissolving the POPTA in the stirred liquid resin under vacuum at room temperature, thereafter adding the 3DCM hardener also at room temperature. All blend solutions were transparent at this stage, indicating complete miscibility at these conditions despite, as shown below, phase separation occurring at lower temperatures. The POPTA content of the overall mixtures was varied from 0 to 25 wt %.

DSC dynamic mode measurements were carried out in a Perkin-Elmer DSC-7 (in a dry nitrogen atmosphere and calibrated with an indium standard) working with 6- to 8-mg samples in aluminum pans. Runnings at constant heating rate of 10°C/min were performed in a temperature range of 30–250°C for every mixture. Measurements at heating rates of 5, 15, and 20°C/min were also conducted. The heat evolved during the reaction of the mixture has been directly determined by integration of the exothermic peaks. For DGEBA/POPTA binary mixtures the T_g was taken as the inflection point in the glass region.

The rheological properties were mainly characterized by dynamic mechanical analysis using a Metravib viscoanalyzer, and working isothermally in annular shearing at a frequency of 10 Hz. The specimen dimensions was usually 4 g. (For comparison measurements were also carried out in a rotational viscometer, Rotovisco Haake RV-20 with around 60 g sampling.)

In order to study the ultimate properties of mixtures prepared with DGEBA with different molecular weights, the mixtures were poured into a preheated mold at 80°C and cured for 2 h, degassing with vacuum during the first hour, and thereafter

Table II Phase Compositions for the DGEBA/POPTA Binary Mixtures

POPTA (%)	T_g (°C)[a]	T_g (°C)[b]	w_1 (%)[a]	w_2 (%)[a]	w_1 (%)[b]	w_2 (%)[b]
0	−13.0	—	100	—	—	—
5	−22.0	−40.0	85.5	14.0	54.7	45.3
10	−21.0	−38.5	87.6	12.4	57.5	42.5
15	−25.0	−40.0	81.1	18.9	54.7	45.3
20	−22.0	−41.5	85.5	14.0	51.9	48.1
50	−25.5	−45.0	80.3	19.7	45.2	54.8
60	−23.0	−51.5	84.4	15.6	32.1	67.9
80	−26.0	−61.5	79.4	20.6	10.4	89.6
100	0	−66.0	—	—	—	0

[a] DGEBA-rich phase.
[b] POPTA-rich phase.

they were postcured at 190°C for 2 h, and allowed to cool gradually to room temperature.

Scanning electron microscopy (SEM) studies have been performed with a JEOL 6400 scanning electron microscope, with an accelerating voltage of 15 kV, by using fracture surfaces coated with a Emscope SC500 gold sputterer.

The dynamic mechanical behavior of the neat and modified epoxy mixtures was studied in the same viscoanalyzer from 20 to 250°C at 3°C/min and 10 Hz by using $60 \times 12 \times 5$ mm³ samples with a bending device. The temperature corresponding to the maximum for the α relaxation, T_α, in the loss factor plotting was also recorded as a measure of the glass transition temperature. The rubber modulus, E'_r, taken as the modulus at $T_g + 40$°C, was used to compare the cross-link density of the networks.

Mechanical measurements were performed in a Instron 4206 test machine equipped with a 5 kN load cell. Flexural properties were carried out at room temperature according to the ASTM D-790 standard at a cross-head rate of 1.7 mm/min using $80 \times 12 \times 5$ mm³ specimens. Fracture toughness tests were made following the European Structural Integrity Society (ESIS) protocol[28,29] using single-edge-notched type samples ($60 \times 12 \times 5$ mm³) in a three-point bending geometry. For both tests a minimum of five specimens were used. The critical stress intensity factor, K_{Ic}, and the critical strain energy release rate, G_{Ic} ($G_{Ic} = [1 - v] K_{Ic}^2 / E$, where v is the Poisson's ratio and E is the flexural modulus), were calculated in this way.

RESULTS AND DISCUSSION

Chemorheology of Curing

POPTA addition to the epoxy resin led to upper critical solution temperature (UCST) behavior.

Condensation problems hindered us the detection of cloud points for the binary mixtures because these occurred at low temperatures. However, the immiscibility of the binary mixtures at low temperatures was proved by cooling the samples into the DSC equipment up to −80°C, and thereafter they were scanned at 10°C/min. Calorimetric studies were only carried out for mixtures cast with the DGEBA provided by Dow Chemical. Table II shows the glass transition temperatures for the mixtures with several POPTA contents. Two T_g appeared for all binary mixtures. The weight fraction of both compounds in each phase can be calculated through Fox equation[30]:

$$1/T_{g \text{ epoxy-rich}} = w_{\text{epoxy}}/T_{g \text{ epoxy}} + w_{\text{POPTA}}/T_{g \text{ POPTA}} \quad (1)$$

where $T_{g \text{ epoxy}}$ and $T_{g \text{ POPTA}}$ are the T_g's of both neat compounds, $T_{g \text{ epoxy-rich}}$ is the T_g of the epoxy-rich phase in the modified mixtures, and w_{epoxy} and w_{POPTA} are the weight fractions of each component in the epoxy-rich phase. Results indicate that the epoxy-rich phase, which T_g appeared around −20/−25°C, remained practically constant independent of POPTA content, and that in the other phase containing both compounds the modifier content increased as higher was the POPTA amount in the overall mixture.

Dynamic mode DSC experiments for neat and POPTA-modified mixtures are shown in Figure 1. As reported in Table III, the maximum exothermic temperature displayed to higher values as POPTA content in the mixture was higher, so showing the dilution effect led by this modifier in the kinetics of curing. In the case of the stoichiometric DGEBA/POPTA mixture no containing 3DCM, the exothermic peak did appear at clearly higher temperatures than for the mixtures cured
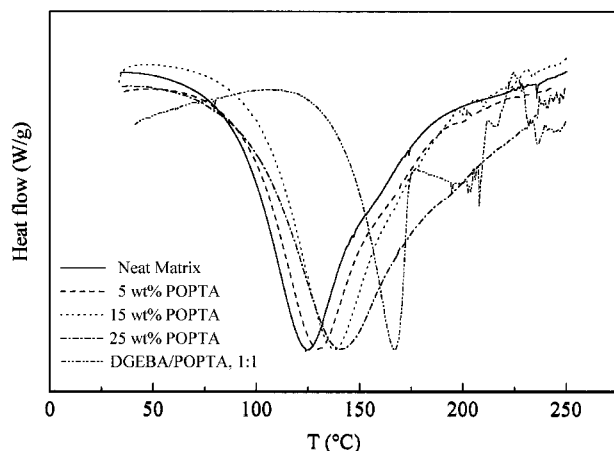
Figure 1 Dynamic thermograms for mixtures with several contents of POPTA.
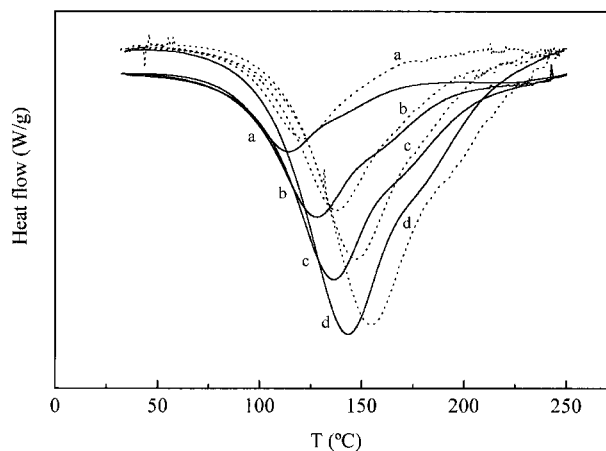

Figure 2 Dynamic scans for the unmodified (—) and the 15 wt % POPTA (...) mixtures at several heating rates. (a) 5°C/min; (b) 10°C/min; (c) 15°C/min; (d) 20°C/min.

with 3DCM. Thereby, it can be considered that, except for high cure temperatures, in the temperature range used for rheological characterization the terminal amine groups of the modifier did practically not react with the epoxy resin. On the other hand, the broadening of the exothermic peak in the dynamic scan at 25 wt % POPTA content seems to indicate that the terminal amine groups of the modifier contributed to chemical reactions in the modified mixtures at high temperatures, and hence possibly the similarity observed in Table III for the heat evolved during reaction.

Figure 2 shows the heat flow evolved during cure at different heating rates for the neat and the 15 wt % modified mixture. The delay on polymerization of the epoxy resin was observed for all heating rates. By using the variation of the temperature corresponding to the maximum on exothermic curve, several methods can be applied to calculate the apparent activation energy for the polymerization of the epoxy resin. In this work

the relation proposed by Kissinger[31] has been used:

$$d(\ln q/T_p^2)/d(1/T_p) = -E_a/R \qquad (2)$$

where q is the heating rate, T_p is the maximum temperature, and E_a is the apparent activation energy. Although the values obtained for E_a can be higher than those corresponding to isothermal curing, they can be qualitatively used for comparison. Thus, in the same way than that reported for other epoxy mixtures,[32–34] E_a values for the neat and the 15 wt % POPTA modified mixtures were 61.5 and 60.3, respectively, indicating that POPTA addition did not modify the kinetics of polymerization, solely exerting a dilution effect leading to higher separation between the reactive chains in the modified mixtures and so, to more difficulties for reaction.

Afterwards, the rheological behavior of mixtures prepared from DGEBA with EE = 175 was investigated. In Figure 3 the dynamic loss modulus, G″, of neat and 15 wt % POPTA modified mixtures with several stoichiometric ratios cured at 80°C is plotted as a function of cure time. In these curves vitrification corresponded to the maximum in G″ because thereafter the rigidity of the forming network leveled off smoothly with increasing time. Moreover, it becomes evident for both modified or not epoxy-rich mixtures that chemical reactions were delayed with respect to those corresponding ones in stoichiometric or hardener-rich mixtures. The dilution effect was
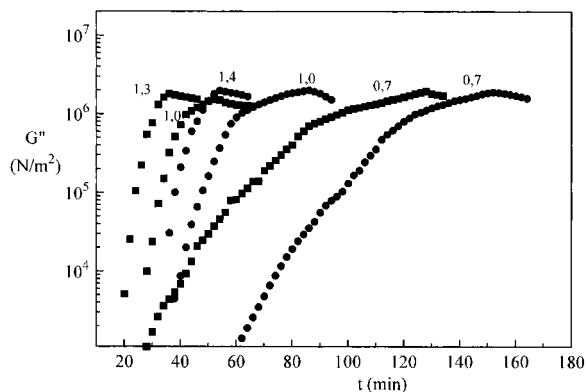
Table III DSC Results Obtained at 10°C/min for POPTA-Modified Mixtures

System	ΔH_{ult} (kJ/EE)	T_p (°C)
DGEBA/3DCM 1 : 1	104	126
DGEBA/3DCM 1 : 1 : 5	106	130
DGEBA/3DCM 1 : 1 : 15	108	136
DGEBA/3DCM 1 : 1 : 25	102	140
DGEBA/POPTA 1 : 1	20.6	166
DGEBA/POPTA 1 : 15	3	184

Figure 3 Loss modulus vs. curing time profiles for unmodified (■) and 15 wt % POPTA-modified (●) mixtures with several stoichiometries.

clear for all stoichiometric ratios as both gelation and vitrification occurred at longer curing times.

Isothermal dynamic measurements have also been performed at several cure temperatures for the neat and POPTA-modified stoichiometric mixtures. In that concerning to gelation through curing, several criteria have been used in the literature survey. Thus, some authors[35–38] have attributed it to the point where the real component, G′, of the dynamic modulus equals to G″, others to the maximum in tan δ,[36,39] and there still are other proposed criteria (performing experiments at several frequencies, tan δ is independent of the frequency at the gelation point,[40] appearance of a shoulder in the G″ curve,[36,41,42] and frequency-independence of the storage modulus at gelation[43]). In this work, times to the gelation region have been arbitrarily taken as time to the maximum in tan δ, $t_{\tan\ \delta}$, and time to the G′-G″ cross-over point, $t_{G'=G''}$. In Table IV times to gelation, t_{gel}, and vitrification, t_{vitr}, for the neat and the POPTA-modified mixtures are shown. At all cure temperatures POPTA addition clearly produced a delay in the happening of gelation and vitrification phenomena.

As shown in Figure 4 a similar delay with POPTA addition was observed for rotational viscometry measurements at 70°C. The formation of an infinite molecular network at the gelation point,[41,44] results in steady-state viscosity becoming infinite, though gelation time is usually taken as time to a finite viscosity of the order of 10^3 – 10^4 Pa.s.[41,45,46] Nevertheless, gelation clearly occurred at lower times for viscosimetric than for dynamic measurements because of the higher exothermy in the first ones due to the different sample sizes used (60 g vs. 4 g).

The overall activation energy of reaction, E_a, has been calculated for both dynamic criteria used for gelation. Nowadays it is well known that at low-cure temperatures polymerization of epoxy resins occurs through reactions between epoxy and primary and secondary amine groups.[47,48]

Table IV   Gelation, Vitrification, and Phase-Separation Times for Neat and POPTA-Modified Mixtures

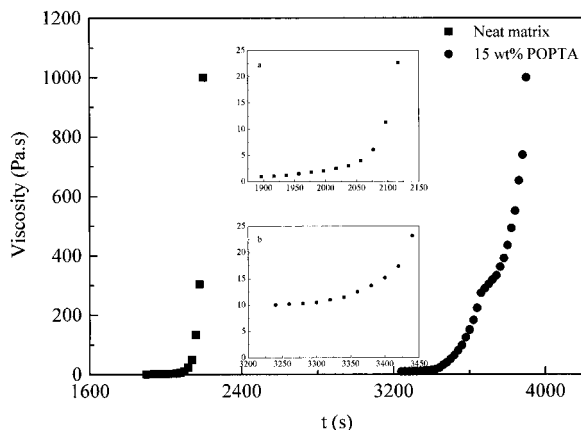| Matrix	T (°C)	$t_{\tan\delta max}$ (min)	$t_{G'=G''}$ (min)	t_{vitr} (min)	t_{cp} (min)	Δt_{cp} (min)
1 : 1	50 (50)	113	146	160	—	—
	60 (59)	69.5	89.5	110	—	—
	70 (68)	50	57.5	78	—	—
	80 (78)	25	38	52	—	—
	90 (87)	13	18	36	—	—
	110 (106)	—	—	23	—	—
	130 (125)	—	—	16	—	—
1 : 1 : 5	80 (78)	32.5	68	80.5	—	—
1 : 1 : 15	50 (50)	201	313	330	—	—
	60 (59)	109	184	225	90	25
	70 (68)	57	118	169	52	12
	80 (78)	42	71	128	38	7
	90 (87)	24	49	90	23	4.5
	100 (97)	16	29	61	13.5	2
	120 (115)	—	—	34.5	—	—
	140 (134)	—	—	27	—	—
	160 (153)	—	—	24.5	—	—
1 : 1 : 25	80 (78)	61.5	75	143	—	—

Figure 4 Viscosity evolution during curing for both neat and 15 wt % POPTA-modified mixtures.

Therefore, these reactions can be described by a kinetically controlled rate equation with an only apparent activation energy:

$$dX/dt = A \exp(-E_a/RT)f(X) \quad (3)$$

By integrating this equation:

$$\ln \int_0^{X\,\mathrm{gel}} [dX/f(X)] = \ln A + \ln t_{\mathrm{gel}} - (E_a/RT) \quad (4)$$

where f (X) is only function of the conversion, X. Because the conversion to the gelation point is constant, the above equation can be rewritten as:

$$\ln t_{\mathrm{gel}} = \mathrm{constant} + (E_a/RT) \quad (5)$$

This Arrhenius approach allows to calculate an overall activation energy of reaction. Values presented in Table V for the neat matrix are similar to those reported in the literature survey.[32,33,49] The E_a for the 15 wt % POPTA-modified mixture was slightly lower than that for the neat matrix, once again indicating that the polymerization delay in the POPTA-modified mixtures was a consequence of the dilution effect produced by modifier addition to the epoxy matrix.

On the other hand, by taking into account the equation proposed by Adabbo and Williams[50]:

$$(T_{g(X)} - T_{g0})/(T_{g0}) = (E - F)X/(1 - (1 - F)X) \quad (6)$$

where $T_{g(X)}$ and T_{g0} are the T_g's for the matrix reacted up to a given conversion X or for the

unreacted resin, respectively, E is the ratio between the network energies of the cross-linked polymer and of the unreacted system, and F is the ratio between chain segment mobilities of the cross-linked and uncross-linked systems. By taking the $T_{g\infty}$ and T_{g0} values (for which X equals to 1 and 0, respectively) measured by DSC ($T_{g\infty}$ and T_{g0} are 455.5 and 256.5 K for the neat epoxy matrix, and 444 and 240 K for the 15 wt % POPTA-modified mixture), E/F ratios of 1.77 and 1.85 have been obtained for the neat and the modified mixture, respectively. Thereafter, by using an approach corresponding to an autocatalytic second order kinetics,[27] times to vitrification can be calculated[51] as:

$$t_{\mathrm{vit}} = (1/A^*)[(\exp A_r/T^*)/(1 + B)]\{(T^* - 1)/$$
$$(E - FT^*) + (1/(1 + B)\ln[(T^* - 1)/B + E$$
$$- 1 + (1 - F)T^*)/(E - FT^*)]\} \quad (7)$$

where T* is an adimensional number equals to T/T_{g0}, A* is the frequency factor, B is the ratio between the catalytic rate constants k_1 and k_2,[27] and A_r is the named Arrhenius number:

$$A_r = E_a/RT_{g0} \quad (8)$$

By calculating the parameters implied in eqs. (6) and (7) by chemorheological studies,[27] the value obtained for the ratio between the chain segment mobilities of the cross-linked and uncross-linked systems, F = 0.39, is equal for both POPTA-modified and unmodified matrix, and it is similar to that presented by Lunak et al.,[32] F = 0.41, for the same unmodified epoxy matrix.

Moreover, the phase separation behavior through curing has been determined by optical microscopy for the 15 wt % POPTA-modified epoxy matrix. In the same way shown by Korkakas et al.,[52] results presented in Table IV indicate that phase separation started before gelation, and

Table V   Apparent Activation Energy Values Obtained by Several Rheological Criteria for Both Neat and 15 wt % POPTA-Modified Mixtures

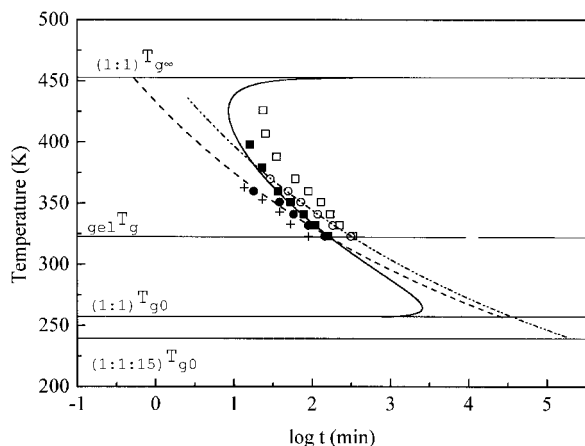| Matrix\Gelation	$t_{\tan\delta\max}$ (min)	$t_{G'=G''}$ (min)	$t_{G''=10^5\mathrm{Pa}}$ (min)
1 : 1	57	54	54
1 : 1 : 15	53	50	51

Figure 5 TTT diagram for both neat (blackfilled) and 15 wt% POPTA-modified mixtures (unfilled). (○) gelation; (□) vitrification; (+) phase separation. Gelation calculated from eq. (5) for neat (- -) and modified (-..-) mixtures. (–) Vitrification of the neat matrix according to eq. (7).

it stopped in the gelation region for all cure temperatures, so showing that morphology was practically defined in this region.

Thus, by using eqs. (5) and (7), the time-temperature-transformation (TTT) diagram for both neat and modified mixtures can be known, as reported in Figure 5, that includes times to phase separation, t_{cp}, for the POPTA-modified epoxy matrix.

The influence of molecular weight of the epoxy oligomer on the rheological behavior was also investigated. For low-molecular-weight neat resins, results reported in Figure 6 indicate that the increase on the epoxy equivalent of the resin practically did not lead to variations in the corresponding gelation times for both neat and POPTA modified mixtures as it occurred for the same epoxy conversion. For the higher EE unmodified or POPTA-containing resin, the sharp increase of loss modulus, or sharp drop in tan δ, corresponding to the gelation region, appeared at lower times. On the contrary, vitrification in the neat mixtures was delayed as higher the molecular weight of the resin was because of the higher hindering for movement of the remaining reacting groups after gelation. On the other hand, the dilution effect produced by POPTA addition was observed for all mixtures, it being independent of the molecular weight of the raw epoxy resin. Nevertheless, in the mixtures containing the higher molecular weight resin the loss modulus followed increasing through curing time. This behavior

could correspond to the lower cross-link density obtained for these mixtures with respect to the others.

Ultimate Behavior

A previous study for 15 wt % POPTA modified DGEBA (EE = 175) mixtures with several amine/epoxy stoichiometric ratios, r,[25] has shown the lowering of small-deformation mechanical properties, but also the toughness improving with respect to those corresponding values for unmodified mixtures. These changes are more remarkable for low amine/epoxy stoichiometric ratios as a consequence of the lower cross-link density of the matrix for these compositions. As the SEM micrographs presented in Figures 7a–d show, al-
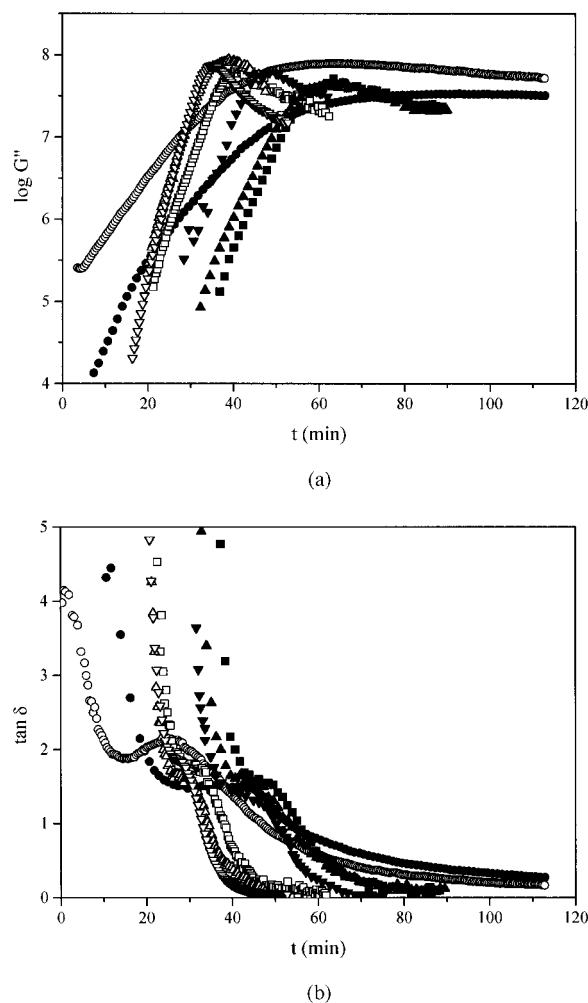

(a)

(b)

Figure 6 (a) Loss modulus and (b) tan δ evolution through curing for neat (unfilled) and 15 wt % POPTA-modified (filled) epoxy matrices prepared from DGEBA with several EE: ▽, 173; △, 188; □, 208; ○ , 375.
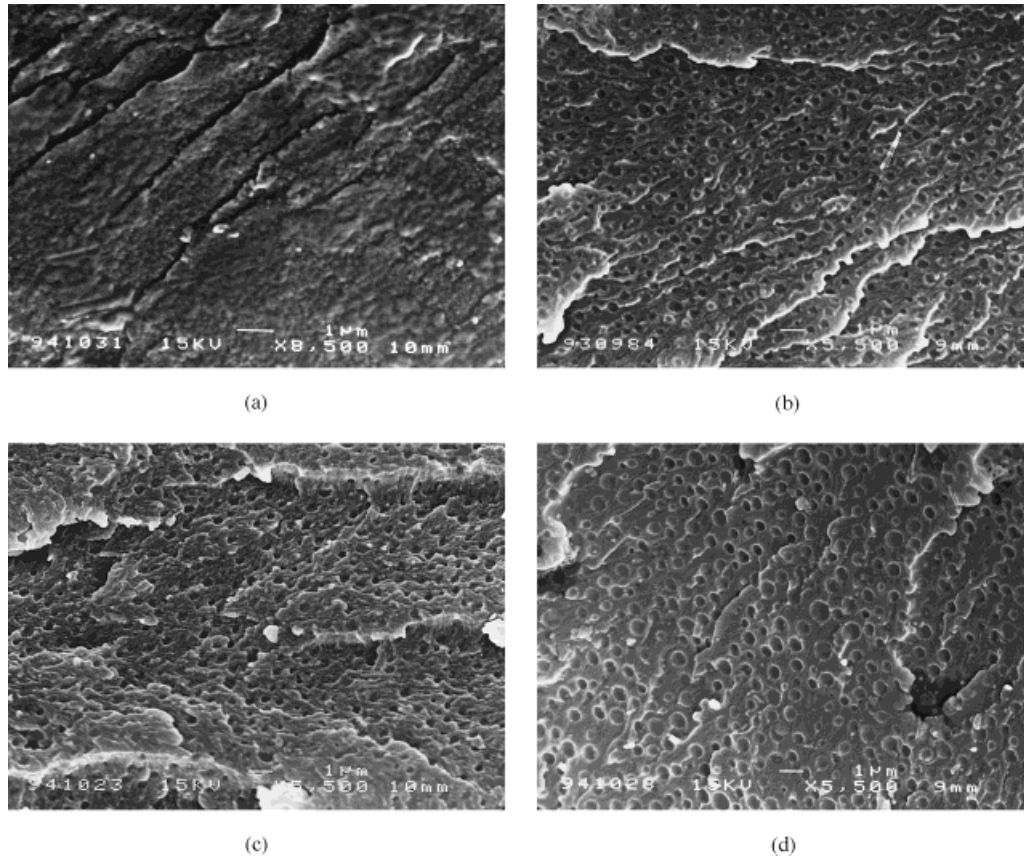
Figure 7 SEM micrographs for mixtures with several stoichiometries modified with 15 wt % POPTA. Stoichiometric ratios: (a) 0.60; (b) 0.80; (c) 1.00; (d) 1.40.

though the particle size obtained for the stoichiometric matrix modified with POPTA oligomer was lower than that shown for the same mixture modified with lithium iodide doped POPTA,[53] the spherical dispersed domains increased in size as amine amount was higher in the matrix formulation. The very small domains observed for the r = 0.60 mixture are possibly a consequence of the delay on polymerization occurring in the precure stage for this stoichiometric ratio, and hence phase separation happened in the 80–190°C stage of curing. So that for this mixture growing of the generated nuclei was stopped because of the high polymerization rate.

From Figure 8 it becomes clear that elastomer-toughening of high cross-linked matrices is more difficult than for lower cross-link density unstoichiometric ones. Anyway, although the molecular weight between cross-links is the controlling factor for this kind of modification, morphology of the matrix can be also an important key for toughness improving. Thus, when mixtures with similar cross-link density, as those for r = 0.90 and r

= 1.40, are compared, the increase on toughness is higher for the amine-rich modified matrix containing bigger elastomer-particles.

Thereafter, in the same way than used by Pearson and Yee,[18] the influence of the molecular
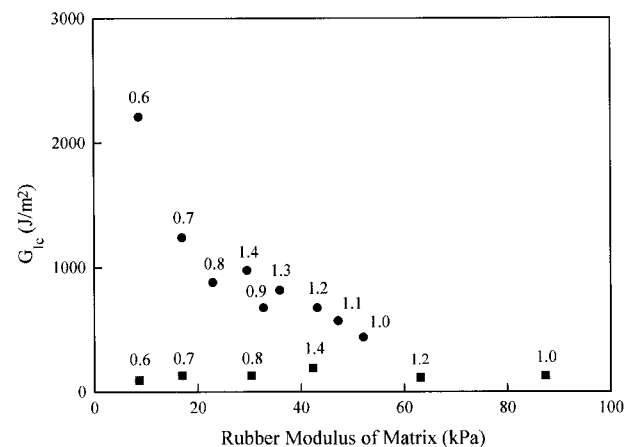

Figure 8 Fracture toughness of unmodified (■) and 15 wt % POPTA-modified (●) mixtures with several stoichiometries (taken from ref. 25).
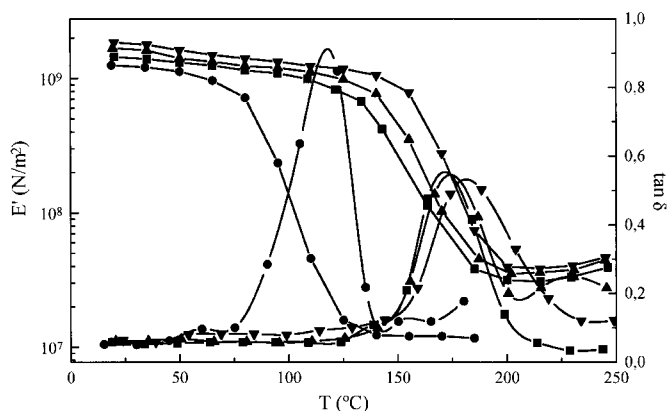
Figure 9 Variation of storage modulus and loss factor upon temperature for 15 wt % POPTA-modified epoxy matrices prepared from DGEBA with several EE: ▼, 173; ▲, 188; ■, 208; ●, 375.

weight of the resin in the dynamic mechanical behavior and ultimate properties has been also investigated for stoichiometric mixtures. As reported in Figure 9 and Table VI, for both 15 wt % POPTA-modified and unmodified mixtures the increase on the epoxy equivalent of the neat epoxy resin led to lower cross-link densities in the cured networks as the rubber modulus, E_r', lowered, and so the molecular weight between cross-links, M_c ($M_c = 3 \, \rho RT / E_r'$, where ρ is the density, R is the gas constant, and T is the temperature), was higher. In the same way, the temperature corresponding to the maximum of the α relaxation, T_α, was lower as molecular weight of the epoxy resin increased. This fact is due to the lower mobility of molecular segments in the tight networks with higher cross-link densities. The mobility increase as the molecular weight of the epoxy resin was higher was also evidenced by the growing height of the α relaxation observed for both neat and modified mixtures.

On the other hand, the clearly lower E_r' values for the modified mixtures with respect to those for

the corresponding neat ones was a consequence of the immiscibility of the mixtures, despite the modifier exerted some influence in the epoxy-rich phase of the modified mixtures as their T_g's also decreased.

Furthermore, the influence of the molecular weight of the resin as well as that for POPTA addition in the mechanical behavior were studied in both kind of mixtures. It is worth noting that all 15 wt % oligomer-modified mixtures yielded whereas the unmodified ones did not so. Figure 10 reports the variation of flexural modulus, E_f, and strength, σ_f, vs. epoxy equivalent of the raw resin. For both type of mixtures, both mechanical properties were nearly constant regardless of the molecular weight of the resin, indicating that for modified mixtures, and even for the unmodified ones, other factors than the cross-link density of the network have an important contribution for definition of small-deformation properties. The clearly lower values shown by the modified mixtures are due to the nil rigidity and strength of the liquid oligomer used.

Finally, fracture toughness measurements were also performed for mixtures performed with several DGEBA oligomers. K_{Ic} and G_{Ic} results are presented in Figure 11. As we have previously shown for POPTA-modified epoxy mixtures,[25–27] oligomer adding clearly improved the toughness of these epoxy matrices but, in a similar way to that reported by Pearson and Yee[18] for rubber-modified epoxy mixtures, the increase was clearly higher for the lowest cross-linked mixture—this corresponds to the higher molecular weight of the uncured resin. These results, along with those previously published for these modified matrices,[25–27] outline the importance of the cross-link density of the matrix, i.e., its ductility, to improve

Table VI Dynamic Mechanical Properties for Both Neat and 15 wt % POPTA-Modified Epoxy Matrices[a]

Resin E.E. (g/eq)	E_r (MPa)	T_g (°C)	$h\alpha$
173	75 (40)	190 (180)	0.60 (0.52)
188	67 (32)	181 (174)	0.78 (0.55)
208	60 (30)	177 (171)	0.77 (0.54)
375	26 (12)	122 (117)	0.95 (0.93)

[a] In parentheses data for the 15 wt % POPTA-modified stoichiometric mixtures.
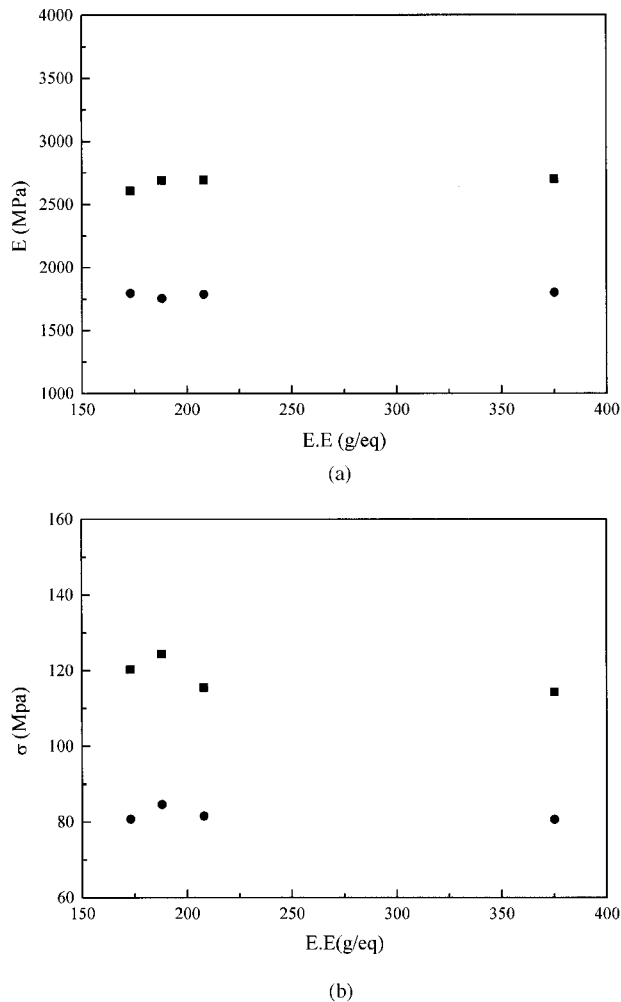
Figure 10 (a) Flexural modulus and (b) strength vs. epoxy equivalent of the DGEBA oligomer for the 15 wt % POPTA modified mixtures (●) and for the neat matrices (■).

the fracture toughness of epoxy matrices by oligomer modification.

CONCLUSIONS

The chemorheology of curing and the ultimate properties of epoxy mixtures modified with a liquid elastomer of medium molecular weight as POPTA have been investigated for a fixed amount of toughening agent. Stoichiometry and molecular weight of the neat resin have been the main keys analyzed.

For the UCST presenting modified mixtures, in the low-cure temperature studied, POPTA only shows a dilution effect in the chemorheology of curing. This behavior is independent of the matrix stoichiometry but also of the molecular weight of the neat resin.

Phase separation occurring before gelation conducted to spherical elastomer particles whose size increased as the amine/epoxy stoichiometric ratio of the matrix was higher. This behavior outlines the importance for controlling the phase separation/polymerization rates ratio.

POPTA modification is effective for matrix toughening but it decreases rigidity and strength of the mixtures. Though the molecular weight of the neat epoxy resin does not clearly influence the small-deformation mechanical properties of both neat and modified stoichiometric mixtures, it controls the cross-link density, and so the thermal behavior of the mixtures. The increasing ductility as lower is the cross-link density of the matrix is a key factor for toughness performance. However, the effectiveness of POPTA as a toughening agent
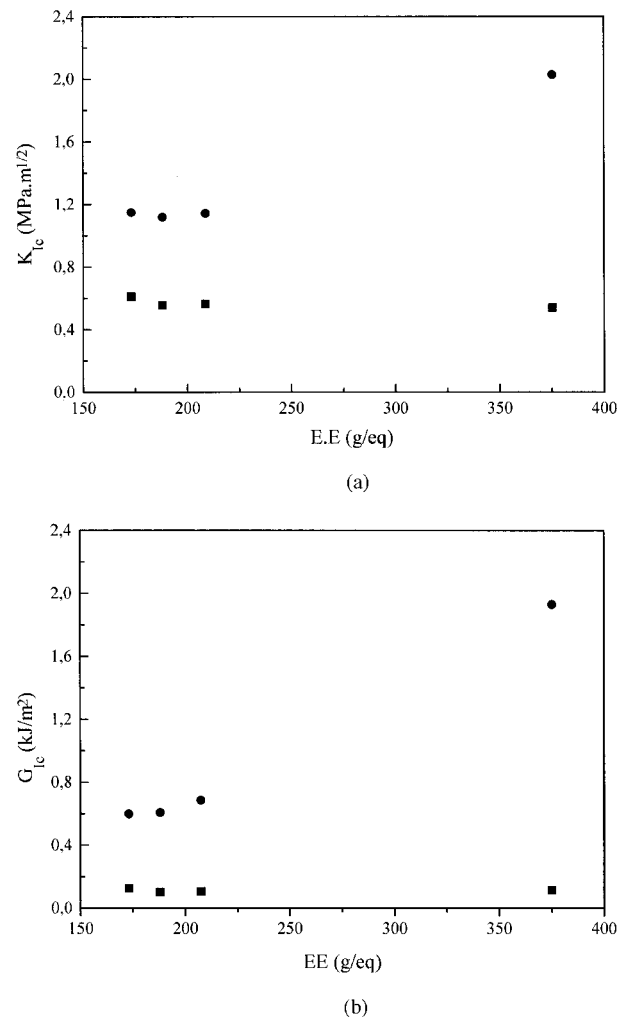

Figure 11 (a) K_{Ic} and (b) G_{Ic} vs. epoxy equivalent of the DGEBA oligomer for the 15 wt % POPTA modified mixtures (●) and for the neat matrices (■).

becomes clear only when the level of cross-linking in the matrix is reduced substantially by increasing the molecular weight of the resin.

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