Rheological, Mechanical, and Morphological Studies of Epoxy/Poly(methyl methacrylate) Semi-Interpenetrating Polymer Networks

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ABSTRACT: Semi-interpenetrating polymer networks (semi-IPNs) of epoxy resin and poly(methyl methacrylate) (PMMA) were synthesized. Methyl methacrylate (MMA) was polymerized by free radical mechanism with azo-bis-isobutyronitrile in the presence of oligomeric epoxy resin (DGEBA), and hexahydrophthalic anhydride as crosslinking agent. The gelation and vitrification transitions during cure/polymerization processes have been examined using parallel-plates rheological technique. From differential scanning calorimetry and rheological techniques, it was suggested that both curing and polymerization processes occur simultaneously. However, the gelation time was longer for the semi-IPN than those observed for the cure of pure DGEBA or polymerization of MMA. The gelation time increased significantly when 5% of MMA was employed, suggesting a diluent effect of the monomer. Higher amount of MMA resulted in a decrease of gel time, probably because of the simultaneous polymerization of MMA during the curing process. Structural examination of the semi-IPNs, using scanning electron microscopy, revealed phase separation in nanoscale size for semi-IPNs containing PMMA at concentrations up to 15%. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3808–3815, 2007

Key words: epoxy; methyl methacrylate; interpenetrating polymer network; morphology; rheology; gel point

INTRODUCTION

Epoxy resins are widely used in a large range of applications, from aerospace structure to dental fillers, because of their excellent properties such as high stiffness, high strength, and good heat and solvent resistance.[1] However, the high level of crosslinking in epoxy networks leads to inherent brittle materials. The incorporation of high performance ductile thermoplastics is one alternative for improving their toughness without sacrificing other useful properties such as stiffness, glass transition temperature, etc.[2–6] There are several studies in literature regarding the use of poly(methyl methacrylate) (PMMA) in blends with epoxy systems.[7–12] Although no toughening effects are normally achieved with PMMA, its choice as a model blend component is because of its solubility in the liquid epoxy resin and its phase separation during subsequent cure of the epoxy matrix. The extent of phase separation depends upon the curing conditions.[13,14]

Another interesting approach to prepare epoxy resin-based blends is through a polymerization or crosslink of one monomer in the presence of another one.[15–19] This process gives rise to the well-known interpenetrating network (IPN) and may produce materials with a number of interesting multiphase morphologies and properties by using appropriate sequence of the network formation. In the sequential technique (seq IPN), the continuous network is constituted by the component, which polymerizes/cures first and dictates the properties, whereas in simultaneous process, the morphology is characterized by a smaller degree of phase separation and, hence, a higher degree of interpenetration.[17]

From an application standpoint, the effective use of any thermosetting system requires the knowledge of physical and kinetic curing mechanisms of the resin and specially the gel point. Accurate determination of the gel point would allow estimating the optimum temperature and time for which the sample should be heated before being allowed to set in the mold. Once the gelation of a resin has occurred, the resin loses its fluidity and cannot be shape-altered thereafter. The gel point for a crosslinking reaction is defined as the instant at which the average molar mass reaches infinity and is characterized by a rapid and exponential increase in viscosity of the medium.

In modified resin systems, the curing process is strongly influenced by the presence of the thermoplastic or elastomer. For example, the addition of carboxyl-terminated copolymer of butadiene and acrylonitrile liquid rubber (CTBN) resulted in a decrease of both gel and vitrification time.[20] However, systems containing polyethersulphone,[21] or poly(methyl methacrylate)[22] presented higher time to gel. The curing process of an IPN system is more difficult to predict because of the complexity of the reactions that take place. In addition, the polymerization may affect the curing kinetics of the epoxy resin or *vice versa*.

The aim of this article is to investigate the rheological changes that occur during the curing process of an epoxy resin and how these changes are affected by the simultaneous polymerization of methyl methacrylate, during the formation of a semi-IPN based on epoxy/PMMA system. The epoxy–amine system normally employed on the development of epoxy networks may be influenced by side reactions between amine and methyl methacrylate monomer via Michael's addition.[23] To avoid this influence, we have chosen anhydride as the hardener for the epoxy resin based on diglycidyl ether of bisphenol A (DGEBA). This curing agent does not interfere on the MMA polymerization and also promotes a slower curing process, compared to amine-based curing agent.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA)-based ER (DER 331) was purchased by Dow Química (São Paulo, Brazil) and presents the following characteristics: $<M_n> = 380$; viscosity = 12,000 cP; epoxide equivalent = 192 g/equiv, as determined by acid titration. The hardener used for the curing process was hexahydrophthalic anhydride containing 1% of an amine catalyst (HY 2123), supplied by Ciba-Geigy (São Paulo, Brazil). Methyl methacrylate, supplied by Metacryl do Brazil, was distilled under reduced pressure and azobis-isobutyronitrile (AIBN) (from Merck, São Paulo, Brazil) was recrystallized from methanol/water.

Synthesis of semi-IPN

DGEBA was first degassed for 60 min in a vacuum oven at 80°C. Then, the anhydride hardener, in a proportion of 1 : 1 weight ratio related to the epoxy resin, was added and the system was continuously stirred until getting a homogeneous solution. Different amounts of MMA with 0.04% of AIBN (related to the MMA content) were added to the epoxy mixtures and further stirred until getting the proper dispersion of MMA monomer. The resulting homogeneous solution was poured into aluminum molds and heated in an oven at 80°C for 4 h, followed by another step heating at 100°C for 4 h and a post curing at 120°C for 6 h.

Characterization and testing

Tensile properties were measured in an Instron 5569 universal testing machine (Boston, MA), at room temperature, according to ASTM D638.

Differential scanning calorimetry was performed using a Thass DSC model XP-10 (Friedberg, Germany). All measurements were made at a scan rate of 10°C/min, in the temperature range of 25–160°C, under continuous nitrogen gas flow. The glass transition temperature (T_g) was recorded after the second heat scan.

Rheological characterization of the systems was carried out using an Anton Par rheometer Physica, model MCR 301, disposed with parallel-plates with a diameter of 25 mm. The oscillatory shear flow measurements were conducted under isothermal and dynamic conditions. For isothermal measurements, the plates were preheated to the isothermal cure temperature and the plate spacing was zeroed. The plates were then separated and the resin sample was rapidly inserted. The plates were then brought back together to a gap of ∼ 0.5 mm. The experiment was initiated when the system returned to the set temperature (∼ 1 min). An angular frequency of 1 Hz and amplitude of 1% were applied. To avoid premature evaporation of the MMA, all samples were preheated at 90°C for 10 min, followed by a quick increase on temperature until the isothermal cure temperature (150, 170, and 190°C). The dynamic tests were performed at 5°C/min from room temperature to 250°C.

Scanning electron microscopy (SEM) was performed in a JEOL JSM-L5300 microscope (Tokyo, Japan), using an accelerator power of 10 kV. The samples were fractured and the surface was treated with
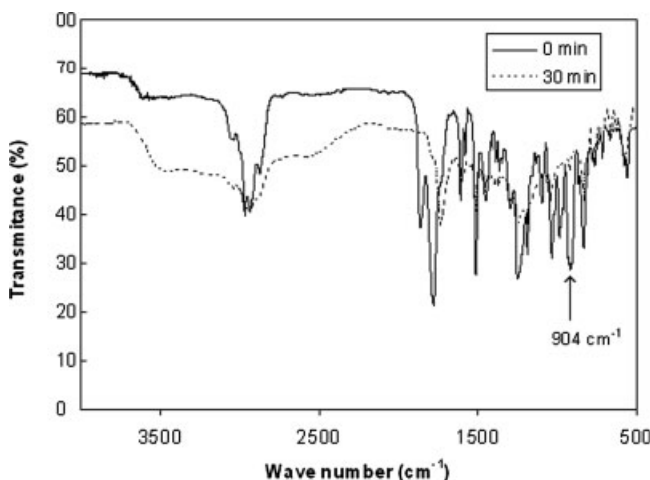

Figure 1 FTIR spectra of a DGEBA/MMA (90 : 10 wt %) mixture (a) before heating (time = 0) and (b) after 30-min heating in an oven.
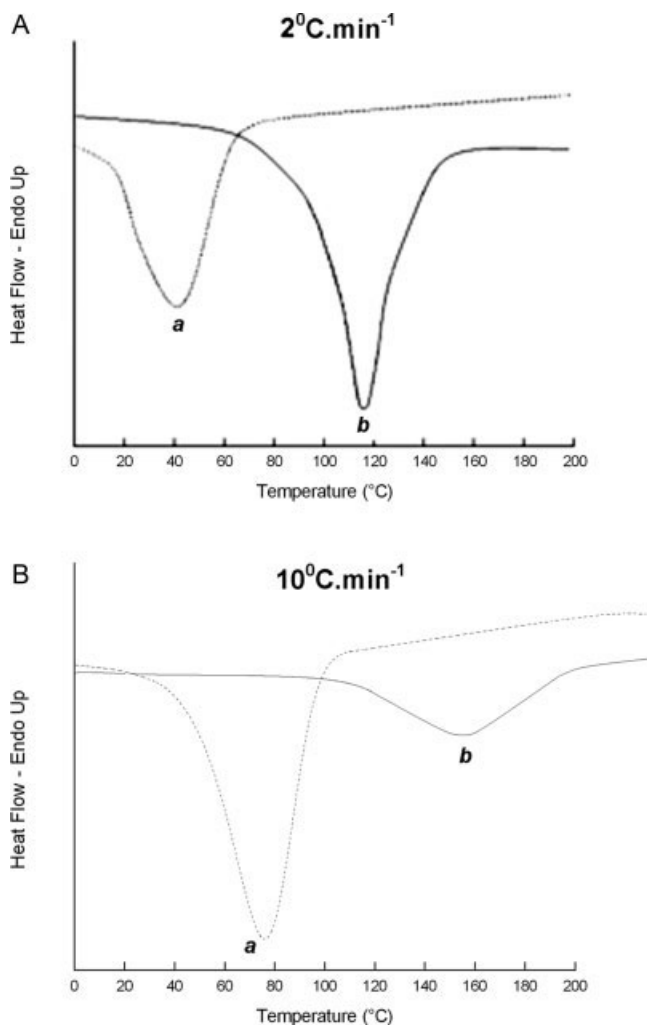
Figure 2 Curves of the dynamic test at the DSC of (a) DGEBA and (b) DGEBA/MMA (90 : 10 wt %) mixture, at heating rates of 2 and 10°C/min.

tetrahydrofuran (THF) for around 15 h at room temperature to extract the PMMA phase. Then, the dried surface was coated with a thin layer of gold and analyzed with the help of a secondary electron detector.

RESULTS AND DISCUSSION

The semi-IPN formation

The formation of DGEBA/PMMA-based semi IPN is a complex process, since different chemical reactions are involved in it, that is, the free radical polymerization of MMA and the curing process of the DGEBA/ anhydride system. In the case of DGEBA curing, gelation and vitrification are the most significant phenomena. The gelation occurs when the reaction products of the DGEBA–anhydride system form a three-dimensional network and the vitrification occurs when the liquid or rubbery reacting mixture is transformed into glassy state as the molar mass increases.

The curing/polymerization process used in this work for the preparation of the semi-IPN started with an isothermal heating at 80°C for 4 h to promote the free radical polymerization of MMA, followed by another heating step at 100°C for 4 h to accelerate the condensation polymerization of DGEBA, and a postcuring at 120°C to finalize the curing process. The initial reaction process was qualitatively followed by FTIR, by spreading the DGEBA/MMA (90 : 10 wt %) mixture containing the corresponding curing/initiator agents on a KBr disk. The disk was submitted to isothermal heating at 80°C in an oven and the FTIR spectra were recorded. Figure 1 illustrates the spectra of a DGEBA/ MMA (90 : 10 wt %) mixture before heating (time = 0) and after 30-min heating in an oven. The symmetric deformation of the cyclic ether group of the epoxy resin at 906 cm^{-1} presented a substantial decrease after 30 min of heating. In addition, the characteristic absorption of carboxyl group, resulted from the reaction between the anhydride and the epoxide or hydroxyl groups of the epoxy resin, increased significantly. These results indicate that during the first step of heating, the DGEBA component started to react. It was impossible to follow the reaction of the MMA in the mixture because the characteristic absorption of the double bond of MMA at 1640 cm^{-1} was masked by the strong absorptions of the carbonyl groups of the anhydride, which appear at 1780–1850 cm^{-1}.

The DGEBA/MMA mixture was also submitted to an isothermal heating at 80°C by using differential scanning calorimetry at a heating rate of 10°C/min. This temperature was chosen for this preliminary study because it corresponds to the first step of the curing cycle used to prepare the IPN. In addition, higher temperature for this first step should contribute for the evaporation of the MMA monomer. No
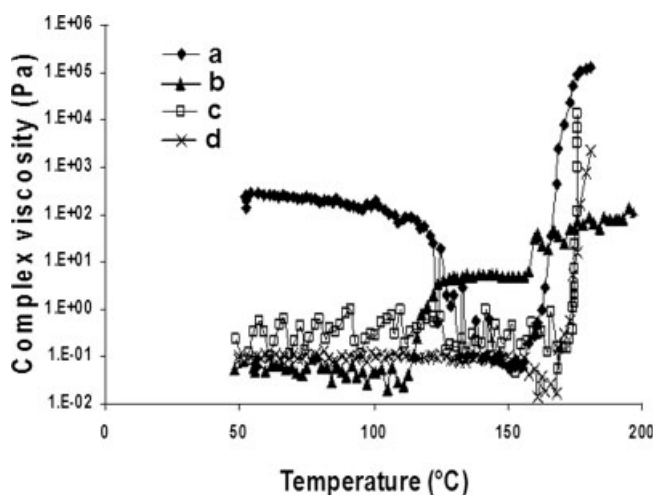

Figure 3 The complex viscosity as a function of temperature for the curing/polymerization of (a) DGEBA, (b) MMA, and the corresponding mixtures with (c) 10% and (d) 30% of MMA.
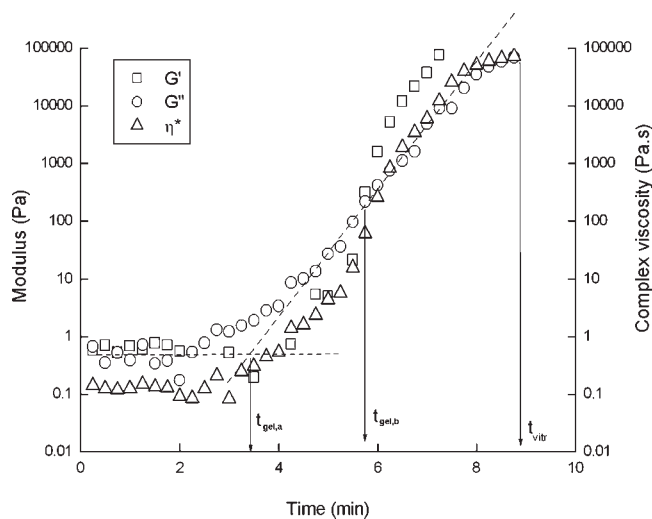
Figure 4 Plots of log storage (G'), log loss (G'') moduli, and complex viscosity (η^*) as a function of time for DGEBA–anhydride system.

significant changes on the heat capacity C_p was observed within 90 min of heating at this temperature. From these preliminary results obtained from FTIR and DSC analyses, one can assume that during this first cycle heating stage, the most important event should be the first step of the DGEBA reaction, involving anhydride and epoxide groups.

To detect the different events involved in the semi-IPN formation (MMA polymerization and DGEBA curing), the curing processes of DGEBA and the DGEBA/MMA (90 : 10 wt %) mixture were followed in nonisothermal conditions by DSC. Figure 2 shows the curve of the dynamic test at the DSC, at heating rates of 2 and 10°C/min. The maximum temperature
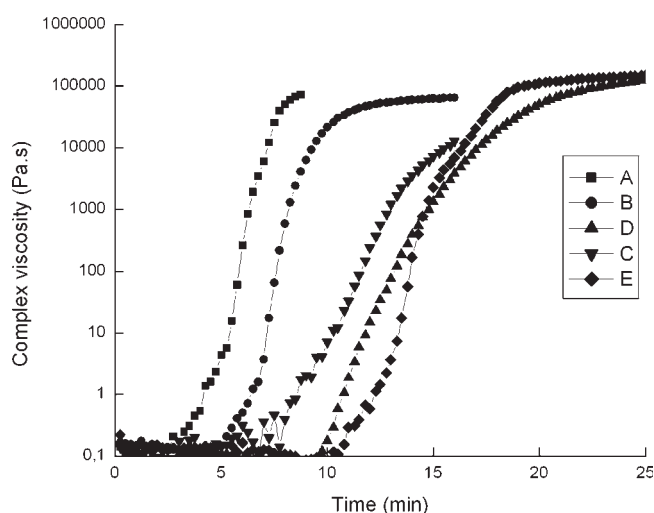

Figure 5 Isothermal complex viscosity at 150°C, as a function of the reaction time for DGEBA/MMA mixtures with (a) 0%, (b) 30%, (c) 20%, (d) 10%, and (e) 5% of MMA content.

of the exothermic peak for the pure DGEBA appeared at 43 and 79°C for experiments performed at heating rates of 2 and 10°C, respectively. The presence of 10% of MMA (Curve b) shifted the curing process toward higher temperature, whose maximum temperature corresponded to 116 or 155°C, depending upon the heating rate. However, the two different processes involved in the IPN formation were not distinguishable, even when the experiments were performed at lower heating rate. These results indicate that both DGEBA curing and MMA polymerization occurred simultaneously when they are blended, and MMA delayed the DGEBA curing processes, and *vice versa*, probably due to the diluent effect of both component related to each other.

Rheological measurements

The cure of a thermoset is characterized by an increase of the molar mass until the development of an ''infinite'' molar mass network. The gelation process gives rise to a considerable increase in viscosity and the development of elastic properties not existing in the pregel resin. In general, the gelation process does not restrain the curing reactions and is difficult to determine directly using techniques receptive only to the chemical reaction, as DSC.[24] Nowadays, the most suitable methods for determining the gel and vitrification time during the curing process of an epoxy system are related to rheometric techniques,[25–29] and for that reason, the parallel-plate rheometry has been chosen in this work to investigate the curing/polymerization behavior during the IPN formation.

The rheological properties during curing/polymerization process were first studied in nonisothermal conditions. Figure 3 compares the viscosity changes with temperature for DGEBA, MMA, and the corresponding mixtures with 10 and 30 wt % of MMA. All systems contain the corresponding curing/initiator agents, in a proportion corresponding to the DGEBA and MMA content in the mixture, respectively. The changes of viscosity for MMA polymerization was significantly lower because the formed polymer was

TABLE I
Gelation and Vitrification Times Obtained from Rheological Experiments for DGEBA/MMA Mixtures as a Function of the MMA Content

DGEBA (%)	MMA (%)	Gelation time (min)		Vitrification time (t_{vitr}) (min)
		$t_{gel,a}$	$t_{gel,b}$	
100	0	3.0	5.7	8.73
95	5	10.4	13.4	24.99
90	10	7.4	9.8	16.08
80	20	9.2	10.7	25.01
70	30	4.9	7.1	16.04

Gelation and Vitrification Times Obtained from Rheological Experiments Under Isothermal Conditions at Different Temperatures, for DGEBA/MMA Mixtures as a Function of the MMA Content

MMA content	Isothermal temperature (°C)									E_a (kcal/J)
	150			170			190			
	$t_{gel,a}$ (min)	$t_{gel,b}$ (min)	t_{vitr} (min)	$t_{gel,a}$ (min)	$t_{gel,b}$ (min)	t_{vitr} (min)	$t_{gel,a}$ (min)	$t_{gel,b}$ (min)	t_{vitr} (min)	
0	2.96	5.75	8.73	2.41	3.06	5.24	1.01	1.72	2.34	56.4
5	10.38	13.44	24.99	7.25	8.34	21.23	4.99	5.63	11.99	100.8
30	4.94	7.10	16.04	4.63	5.53	9.22	2.10	3.92	8.52	43.8

in the melting state at the temperature corresponding to the increase of the viscosity. At the beginning of the heating process, the viscosity of the DGEBA (Curve a) was high when compared to the mixtures with MMA because of the higher viscosity of the former. As the temperature increased, the viscosity decreased due to the melting of the resin and reached a minimum. As the amount of MMA increased in the sample, the viscosity of this initial heating stage was lower because of the lower viscosity of the MMA monomer.

At a defined temperature, the viscosity increased exponentially as a consequence of the curing/polymerization processes. The MMA polymerization started around 110°C (Curve b), that is, at lower temperature than the DGEBA curing, which was found to be around 158°C. The reaction processes that occurred during the rheological experiments of DGEBA/MMA mixtures started at a little higher temperature (around 175°C). These results are in agreement with those obtained from nonisothermal DSC experiments and confirm that both DGEBA curing and MMA polymerization processes during the IPN formation are delayed by the presence of the different reaction processes operating simultaneously.

The rheological behavior during the curing process is normally studied under isothermal conditions. Figure 4
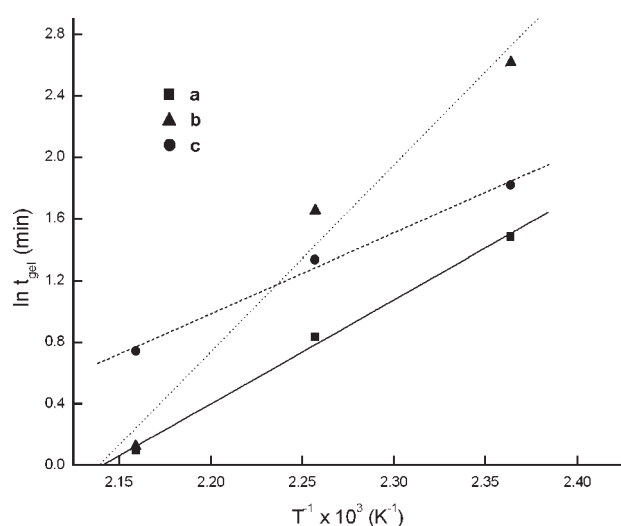
shows the typical change in storage (G') and loss (G'') moduli, and the complex viscosity (η^*) as a function of time for DGEBA–anhydride system. The region of interest in these curves corresponds to that in which the G' and G''' values increase exponentially versus time, where the gelation and, therefore, the crosslinking occur. The gel time has been determined according to the more commonly used criteria: (a) at the point that corresponds to the crossing between the baseline and the tangent drawn at the yield point in the modulus G'' curve[26,27] ($t_{gel,a}$) and (b) at the point corresponding to the crossover between G' and G'' curves ($t_{gel,b}$).[26,28] The vitrification time (t_{vitr}) has been determined as the time corresponding to the maximum G'' peak.[29]

The isothermal complex viscosity at 150°C, as a function of the reaction time is plotted in Figure 5 as a function of MMA concentration. The results related to the vitrification and gelation times are summarized in Table I. The presence of 5% of MMA in the mixture resulted in a substantial increase of the gel and vitrification times, which may be attributed to a diluent effect of MMA, which retards the curing process of DGEBA. It is interesting to observe that by increasing the MMA concentration in the mixture, the gelation time decreased. This behavior may due to the MMA polymerization contribution. Therefore, higher amount of MMA in the system should contribute for a decrease of the gel time. From these results, one can assume that the gelation time observed from rheological experiments performed at isothermal conditions involves both the DGEBA curing and also the MMA polymerization.

The effect of MMA concentration on the gelation time was studied at different temperatures. Table II

Figure 6 Dependence of ln (t_{gel}) versus $1/T$ for (a) DGEBA, and their mixtures with (b) 5% and (c) 30% of MMA.

TABLE III
Thermal Data Obtained from DSC of the Postcured Epoxy/PMMA Semi-IPN

Semi-IPN component (wt %)		Glass transition temperature range (°C)	T_g (°C)
Epoxy network	PMMA		
100	0	121–131	126.0
95	5	121–131	125.9
90	10	120–131	125.8
85	15	121–131	126.4
70	30	117–133	124.8
0	100	111–129	120.0

TABLE IV
Tensile Properties of Epoxy/PMMA Semi-IPNs

Semi-IPN component (wt %)		Ultimate tensile stress (MPa)	Elongation at break (%)	Young modulus (MPa)
Epoxy network	PMMA			
100	0	72.6 ± 3.8	2.6 ± 1.1	5200 ± 188
95	5	79.8 ± 3.5	4.0 ± 1.0	5100 ± 173
90	10	72.8 ± 0.7	3.5 ± 0.5	4800 ± 380
85	15	70.0 ± 1.6	4.0 ± 1.0	5000 ± 100
70	30	54.6 ± 1.7	3.2 ± 0.1	4600 ± 315

presents the results related to gelation and vitrification times of DGEBA and their mixtures with 5 and 30% of MMA, taken at three different temperatures: 150, 170, and 190°C. The temperature-independent activation energy (E_a) for the curing/polymerization processes can be calculated by the Arrhenius approach, which involves the best fit of the ln (t_{gel}) versus inverse temperature. Figure 6 illustrates the dependence of ln (t_{gel}) versus $1/T$ for DGEBA, and their mixtures with 5 and 30% of MMA. Pure DGEBA presented an E_a equal to 56.4 kcal/J. The presence of 5%

of MMA increased this parameter significantly (to 100.8 kcal/J), whereas 30% of MMA decreased this parameter, reaching a value lower than pure DGEBA. The decrease of E_a with high MMA content suggests a simultaneous polymerization of MMA with the DGEBA crosslink.

Properties of the semi-IPN networks

The effect of the PMMA content on glass transition temperature of the semi-IPNs is summarized in Table III.
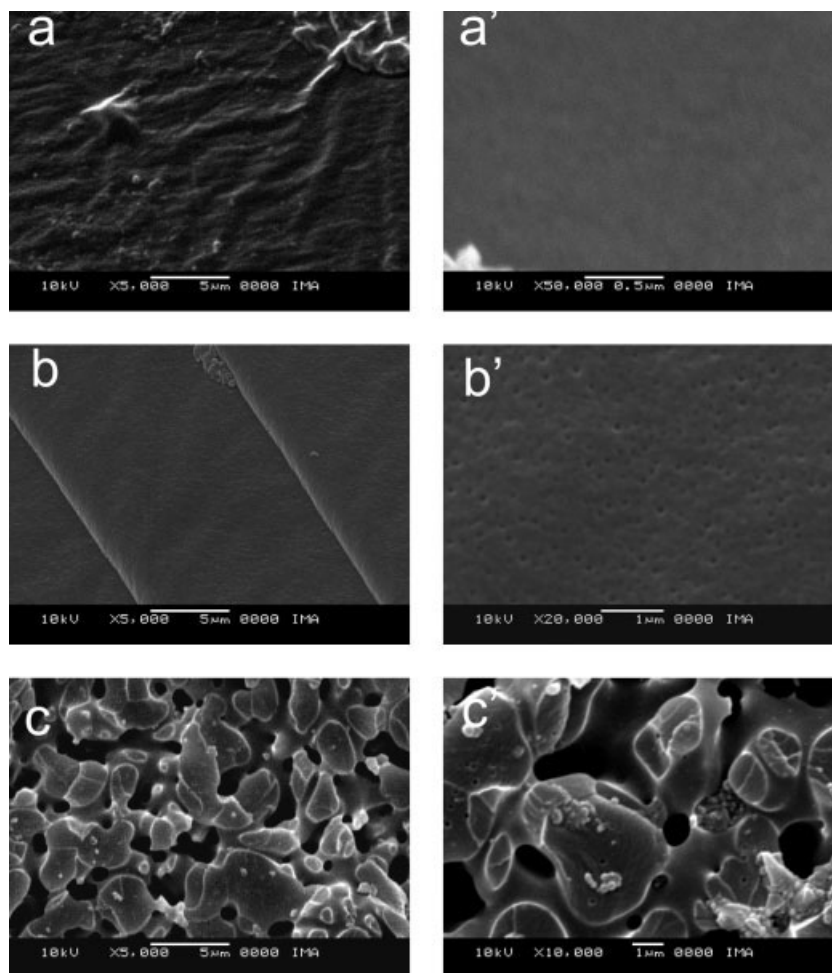

Figure 7 SEM micrographs of epoxy networks with (a) 5%, (b) 15%, and (c) 30% of PMMA. (a′, b′, and c′ are the corresponding micrographs taken at higher magnification.)

These values were taken from the second DSC scan, using post-cured samples. All compositions displayed single T_g. For systems containing up to 16% of PMMA, the T_g values were almost similar to that found for the neat epoxy network. Higher amount of PMMA (>16%) resulted in a slight decrease of T_g values and also a broadening of the transition range. However, it was impossible to distinguish the PMMA and epoxy network phase transitions because the T_g values of the components are very close (120 and 126°C, respectively).

The tensile parameters of the semi-IPN are summarized in Table IV. The presence of PMMA in a concentration up to 5% resulted in slight increase on both tensile strength and elongation at break. Further increase of PMMA content in the semi-IPN did not result in any significant change on the mechanical properties, except for the system containing 30% of PMMA, when a significant decrease of ultimate tensile strength and modulus was observed, probably because of phase-separated morphology associated to the brittle nature of both components.

Figure 7 compares the SEM micrographs of these materials as a function of the composition. The fracture surface was treated with THF for 15 h at room temperature to extract the PMMA phase. The IPN containing 5% of PMMA presented a homogeneous morphology with no distinguishable phase separation, even at a magnification corresponding to 50,000 times [Fig. 7(a′)]. Semi-IPN containing 15% of PMMA presents very small domains with particle size in the order of 50–100 nm, as observed in Figure 7(b,b′). Both samples are completely transparent, indicating that the size of the domains is smaller than the wavelength of the visible light (380–780 nm). Physical blends of PMMA and epoxy network, reported in literature, presented phase-separated morphology induced by the curing process, whose domain size stayed in the range of 1–20 μm.[22] The morphology with very small particle size of PMMA domains for semi-IPN network containing up to 15% of PMMA suggests the simultaneous polymerization/curing process, as reported in literature,[17] and agrees with the rheological behavior. Higher amount of PMMA in the semi-IPN (30%) resulted in a heterogeneous blend with gross phase-separated morphology, as expected for immiscible blend [Fig. 7(c)]. In addition, there are some small holes inside the epoxy phase, indicating subinclusions of PMMA particles inside this phase. In spite of the long time of extraction, the micrograph of this IPN still presents some portion of nonextracted PMMA (white regions inside the epoxy phase), probably because of the high PMMA concentration in this phase.

CONCLUSIONS

Semi-IPN networks constituted by epoxy–anhydride and PMMA were studied as a function of the PMMA content. From the results observed in this article, one can conclude that:

- The presence of MMA during the semi-IPN formation shifts the cure temperature of the system toward higher value, which was attributed to the diluent effect of MMA. This behavior was observed from nonisothermal DSC and rheological experiments.
- The low amount of MMA (5%) resulted in a significant decrease of the gelation time because of the diluent effect of the monomer. However, increasing the amount of MMA resulted in a decrease of the gelation time, indicating that both polymerization and curing processes are responsible for this behavior.
- Both polymerization and curing processes occur simultaneously, indicated by both DSC and rheological experiments. This behavior contributes for a morphology characterized by very small particle size of the PMMA domain for semi-IPN containing up to 15% of PMMA. These samples are completely transparent, indicating that PMMA phase is dispersed as nanoparticles inside the epoxy matrix.

References

1. May, C. A. Epoxy Resins. Chemistry and Technology; Marcel Dekker: New York, 1988.
2. Hourston, D. J.; Lane, J. M.; Zhang, H. X. Polym Int 1997, 42, 349.
3. Bucknall, C. B.; Patridge, I. K. Polymer 1983, 24, 639.
4. Williams, R. J. J.; Rozenberg, B. A.; Pascault, J. P. Adv Polym Sci 1997, 128, 95.
5. Venderbosch, R. W.; Meijer, H. E. H.; Lemstra, P. J. Polymer 1994, 35, 4349.
6. Venderbosch, R. W.; Meijer, H. E. H.; Lemstra, P. J. Polymer 1995, 36, 1167.
7. Woo, E. M.; Wu, M. N. Polymer 1996, 37, 2485.
8. Hseih, H. K.; Woo, E. M. J Polym Sci Part A: Polym Phys 1996, 34, 2591.
9. Mondragon, I.; Remiro P. M.; Martin, M. D.; Valea, A.; Franco, M.; Bellenguer, V. Polym Int 1998, 47, 152.
10. Galante, M. J.; Oyanguren, P. A.; Andromaque, K.; Frontini, P. M.; Williams, R. J. J. Polym Int 1999, 48, 642.
11. Ritzenthaler, S.; Girard-Reydet, E.; Pascault, J. P. Polymer 2000, 41, 6375.
12. Remiro, P. M.; Riccardi, C. C.; Corcuera, M. A.; Mondragon, I. J Appl Polym Sci 1999, 74, 772.
13. Jansen, B. J. P.; Meijer, H. E. H.; Lemstra, P. J. Polymer 1999, 40, 2917.
14. Remiro, P. M.; Marieta, C.; Riccardi, C. C.; Mondragon, I. Polymer 2001, 42, 9909.
15. Frisch, H. L.; Frisch, K. C.; Klempner, D. Pure Appl Chem 1981, 53, 1557.

16. Sperling, L. H. Interpenetrating Polymer Networks and Related Material; Plenum: New York, 1981.
17. Sands, J. M.; Jensen, R. E.; Fink, B. K.; Mcknight, S. H. J Appl Polym Sci 2001; 81: 530.
18. Chakrbarty, D.; Das, B.; Roy, S. J Appl Polym Sci 1998, 67, 1051.
19. Alcântara, R. M.; Pires, A. T. N.; Barros, G. G.; Belfiore, L. A. J Appl Polym Sci 2003, 89, 1858.
20. Calabrese, L.; Valenza, A. Eur Polym J 2003, 39, 1355.
21. McKinnon, A. J.; Jenkins, S. D.; McGrail, P. T.; Pethrick, R. A. Macromolecules 1992, 25, 3492.
22. Gomez, C. M.; Bucknall, C. B. Polymer 1993, 34, 2111.
23. Titier, C.; Pascault, J. P.; Taha, M.; Rozenberg, B. J Polym Sci Part A: Polym Chem 1995, 33, 175.
24. Regueira, L. N.; Fernandez, C. A. G.; Barreiro, S. G. Polymer 2005, 46, 5979.
25. Laza, J. M.; Julian, C. A.; Larrauri, E.; Rodriguez, M.; Leon, L. M. Polymer 1998, 40, 35.
26. Gillham, J. K.; Benci, J. A. J Appl Polym Sci 1974, 18, 951.
27. Apicella, A.; Nicolais, L.; Iannone, M.; Passenini, P. J Appl Polym Sci 1984, 29, 2083.
28. Tung, C. Y. M.; Dynes, P. J. J Appl Polym Sci 1982, 27, 569.
29. Lange, J.; Altmann, N.; Kelly, C. T.; Halley, P. J. Polymer 2000, 41, 5949.