Design of Morphology in PMMA-Modified Epoxy Resins by Control of Curing Conditions. I. Phase Behavior

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ABSTRACT: Rheokinetic and phase separation behavior of diglycidylether of bisphenol-A-4,4'-diaminodiphenyl methane epoxy mixtures, modified with a constant amount (15 wt %) of poly(methyl methacrylate) (PMMA), have been investigated. Stoichiometric epoxy/amine mixtures precured at 80°C several times presented various levels of miscibility. Differential scanning calorimetry (DSC) and dynamic mechanic thermal analysis were used for rheokinetic studies of curing and also for testing the thermal behavior of the fully cured mixtures. Phase separation, through curing, was simultaneously studied by transmission optical microscopy and DSC, showing an excellent correlation between the results obtained with both techniques. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 772–780, 1999

Key words: phase behavior; morphology; cure kinetics; epoxy resin; poly(methyl methacrylate)

INTRODUCTION

Most investigations on thermoplastic modification of thermosetting matrices have focussed on the influence of factors, such as the modifier content,¹⁻⁸ but also on terminal groups for better interphasing,⁹⁻¹¹ though the latter is not so clear for improving toughness.¹¹⁻¹⁴

However, not much work has studied the relationship between phase separation and the matrix polymerization rates.^{15–17} These studies usually use a catalyst to increase the rate of curing. Nevertheless, for some systems, the possibility of obtaining different morphologies in the cured mixtures by only modifying molding parameters, such as temperature and time of curing, could be an interesting way to investigate. We have already tested this idea by only controlling precure temperature in polysulfone-modified epoxy mixtures¹⁸ with good results.

We have previously reported on the dynamic mechanical behavior of epoxy resins modified with several amounts of poly(methyl methacrylate) (PMMA), showing several levels of apparent miscibility as a function of the thermoplastic content in the mixtures.¹⁹ In this study, the influence of precuring time, firstly, on the rheokinetics at curing, and, secondly, on the phase separation

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behavior of diglycidylether of bisphenol-A (DGEBA)– 4,4'-diaminodiphenyl methane (DDM) stoichiometric mixtures containing 15 wt % of PMMA have been investigated. The importance of the occurrence of gelation, simultaneous with phase separation, in the definition of the final microstructure has been analyzed.

EXPERIMENTAL

The epoxy resin used was DER-332, a DGEBA, kindly supplied by Dow Chemical. It has an epoxy equivalent weight EE of around 175 and a hydroxyl/epoxy ratio close to 0.03. The curing agent was DDM (HT-972, kindly supplied by Ciba-Geigy). PMMA (Altuglas GR 9E, Elf Atochem) had a M_n equal to 58,000, as measured by gel permeation chromatography (GPC) in a Waters 150-C ALC/GPC instrument equipped with 3 columns PLGel of 500, 104, and 106 A, from Polymer Labs.

The thermoplastic-modified mixtures were prepared in the following way. First, a weighted amount of PMMA was dissolved in dichloromethane to give an approximately 10 wt % solution. DGEBA was then added to the solution and stirred until complete dissolution of the resin. The solvent was removed afterwards by heating at 80°C *in vacuo;* and DDM, in a stoichiometric amine/epoxy ratio, was added and dissolved by continuously stirring the mixture for 5 min. The final amount of PMMA in the DGEBA–DDM matrix was 15 wt %. At this stage, all blend solutions were transparent, thus indicating complete miscibility.

The mixtures were submitted to a curing program consisting of the following three steps: a precuring at 80°C for times from 2 to 7 h, a secondary curing stage at 140°C for 1.5 h, followed by postcuring at 200°C for 2 h.

Transmission optical microscopy (TOM) measurements were performed with a Olympus BHT-M microscope equipped with a photoelectric cell. Scans were carried out isothermally at various temperatures. Cloud points were not observed at temperatures as high as 200°C.

1-2 g of uncured DGEBA-DDM-15 wt % PMMA mixture were poured into aluminum caps and cured in an oven at 80°C. After fixed periods of time, the samples were taken out from the oven and were quickly cooled in a refrigerator. Calorimetric and solubility measurements were performed on these samples.

Gelation times were measured by dissolving the quenched samples, cured for different times at 80°C, in dichloromethane. Gelation time was taken as the time at which the first insoluble fraction was detected.

Differential scanning calorimetry (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 6–8 mg samples in aluminum pans. Runs at a constant heating rate of 10°C/min were performed in a temperature range from 30 to 250°C. The glass transition temperature T_g was taken in a second scan as the middle point of the endothermic shift in the DSC scan.

Kinetic studies were performed with the DSC equipment working isothermally at several temperatures. Conversion was taken as the enthalpy recorded in the isothermal scan at each cure time, divided by the total enthalpy obtained in a dynamic run.

The dynamic mechanical behavior of the neat and modified epoxy mixtures was studied in a Rheometrics DMTA equipment in the single cantilever mode. Temperature scans from 40 to 250°C at 3°C/min and 1 Hz were performed, using $25 \times 12 \times 2$ mm³ specimens. The temperature corresponding to the maximum for the α relaxation T_{α} in the loss factor plotting was recorded as a measure of the glass transition temperature.

RESULTS AND DISCUSSION

DGEBA-DDM-PMMA 1/1/15 wt % mixtures were visually observed after each of the curing steps in a preheated mold. All samples were transparent after the curing period at 80°C. However, after the secondary curing at 140°C, the samples that had been cured for 2 or 3 h at 80°C became opaque, but those samples cured longer at 80°C remained transparent. No change in the transparency state was observed after the postcuring period at 200°C.

In the same way, the above mixtures were precured for 3 h at temperatures ranging from 70 to 140°C. Excepting the mixture precured at 120°C, which was translucent, and the mixture precured at 140°C, which was opaque, all the others were transparent after precuring. Mixtures containing 5 or 10 wt % PMMA precured at 140°C were also translucent. At precuring temperatures higher than 140°C, mixtures containing up to 15 wt % PMMA appeared completely phase-separated.

Sample	Precuring Time (h)	$T_{g1}(^{\circ}\mathrm{C})$	$\Delta T_{g1}(^{\rm o}{\rm C})$	$T_{g2}(^{\rm o}{\rm C})$	$\Delta T_{g2}~(^{\rm o}{\rm C})$	Appearance
DGEBA–DDM–PMMA 1/1/15%	2	116.6	9.4	157.3	10.9	opaque
	3	116.2	10.0	165.8	15.0	opaque
	5			153.7	25.0	transparent
	6		_	152.7	22.9	transparent
	7			153.5	22.6	transparent
DGEBA–DDM 1/1	3			183.1	18.2	transparent
PMMA		113.8	16.3	—	—	transparent

Table I Glass Transition Temperatures T_g and Width of the Transitions ΔT_g for the Postcured Plaques, Precured for Different Times at 80°C

The glass transition temperatures, measured in the second DSC scan, of the postcured plaques containing a 15 wt % PMMA precured at 80°C are shown in Table I, where the T_g 's of the neat matrix and that of pure PMMA are also collected for comparison. As can be seen, the opaque plaques showed two distinct glass transitions. The higher T_g can be attributed to an epoxy-rich phase, and the lower one is reasonably ascribed to a PMMA-rich phase. However, the temperatures of these two transitions were not coincident with those for neat epoxy matrix and pure PMMA, indicating that these phases were not pure or, maybe, that in the epoxy-rich phase of these mixtures, a crosslinking density different to that for the neat matrix was attained. In addition, the glass transition of the mixtures precured for longer times appeared wider than that for the opaque mixtures, suggesting incomplete miscibility of these transparent mixtures.

The transparent plaques containing 15 wt % PMMA showed only one T_g that was similar for the three samples precured to long times. The temperature at which this transition appeared was lower than the T_g for the neat matrix. The presence of PMMA, itself having a lower T_g than the cured epoxy, can in effect decrease the T_{σ} of this phase. Nonetheless, by applying the Fox equation,²⁰ frequently used to calculate the T_g in miscible polymer systems, a T_g of 171.2°C, higher than the measured T_g , is obtained. This result seems to indicate that other factors must also be affecting the observed $T_{g}.$ One of these factors could be the existence of a lower crosslinking density in the epoxy-rich phase than that corresponding to the neat matrix. However, the similarity in the T_g 's of the three transparent samples suggests that, despite the different curing times, all of them had reached a similar crosslink density.

Dynamic mechanical thermal analysis (DMTA) bending measurements, reported in Figure 1, pre-

sented similar trends. Thus, the 15-wt % PMMAmodified mixtures precured for 2 or 3 h at 80°C showed two α relaxations, the high-temperature one corresponding to an epoxy-rich phase, and the low-temperature one in the region of the α relaxation of PMMA. However, this technique yields more information than DSC about the composition of the separated phases. As can be seen, the mixtures precured for 5, 6, or 7 h at 80°C showed the α relaxation at similar temperature. Moreover, the height and width of these peaks were similar to the height and width of the peak corresponding to the α relaxation of the unmodified epoxy, which appeared at higher temperatures. Besides, these mixtures showed a small shoulder in the region of the α relaxation of PMMA, which could correspond to rather small PMMA particles. On the other hand, the modified mixtures precured for 3 h gave the α relaxation at higher temperatures than those precured for longer times. This fact indicates that less PMMA was dissolved in the epoxy-rich phase. Moreover, the higher temperature and width corresponding to the α relaxation of the mixture precured for 3 h at 80°C in comparison to these values for the mixture precured for 2 h at 80°C lead one to suppose that some stoichiometric imbalance appeared as a consequence of phase separation. It has been observed by infrared (IR) spectroscopy¹⁹ that DDM strongly interacts with PMMA. Thus, this stoichiometric imbalance could correspond to the preferential migration of DDM to the PMMA phase or, because of the higher functionality of DDM with respect to DGEBA, which could cause a greater unreacted DGEBA concentration at any given extent of reaction, DGEBA could migrate to the PMMA phase.

By taking into account the above experimental evidence, and also the higher height observed for the α relaxation of the mixture precured for only 2 h, phase separation could be explained in the



Figure 1 Tan δ versus temperature for the DGEBA–DDM–15 wt % PMMA postcured plaques, precured for different times at 80°C. A detail of the low-temperature transition can be seen in the upper left corner: (**I**) 2, (\diamond) 3, (**O**) 5, (**D**) 6, and (\diamond) 7 h; (**O**) DGEBA–DDM 1/1.

following way: as the mixture precured for 3 h at 80°C was very close to gelation, phase separation, which happened in the gelation region, took place while the mixture was being heated to 140°C. For the mixture precured for 2 h, phase separation possibly occurred once 140°C was reached in the secondary stage of curing. Therefore, for the 3-h precured mixture, time for the phase separation process, which, as a first approximation, takes place up to gelation, should be longer than for the 2-h precured mixture so that the epoxy-rich phase of the former mixture should contain less PMMA.

The thermal behavior of the quenched samples precured several times at 80°C was analyzed by DSC. The results are shown in Figure 2. At temperatures above the glass transition, an exothermic peak appeared as a result of the progress of curing reactions that were stopped by quenching. The glass transition temperatures of the quenched samples measured in the first scan are collected in Table II. For curing times shorter than 180 min, the glass transition temperatures of the samples were lower than the starting temperature of the calorimetric scan; but for longer times, the T_g continuously increased with curing time until it reached a plateau for curing times longer than 285 min because vitrification had happened. The highest T_g values obtained are slightly higher than the precuring temperature used as a consequence of the existence of some reactions via diffusion after vitrification.

Once vitrification had taken place, the curing reactions were almost stopped, so a longer curing time would not yield greater conversion. When heated to a temperature higher than the T_g , the polymerization reaction will start again. For this reason, the three plaques precured for 5, 6, or 7 h at 80°C, and later submitted to the full cure schedule, had identical T_g 's.

With the aim of understanding the dissimilar behavior of mixtures precured for different times at 80°C or precured at different temperatures, the kinetics of network formation in the presence of PMMA and the phase separation process may be analyzed.

Although several simultaneous reactions can occur during the polymerization process, the overall extent of reaction x is generally obtained by



Figure 2 DSC traces for the modified DGEBA–DDM–15 wt % PMMA precured for different times at 80° C.

assuming the proportionality between x and the heat evolved during curing referred to as total heat of reaction $(-\Delta H_T)$. Total heat of reaction was determined by dynamic runs in DSC performed at 10°C/min as 99.7 ± 1.7 and 100.5 ± 1.4 kJ/eq for the pure and modified system, respectively. Figure 3 shows the corresponding thermograms expressed as dx/dT versus temperature. As can be seen, PMMA addition delayed polymerization of the epoxy resin, and a shoulder ap-

peared after the peak temperature. Isothermal thermograms, expressed as rate of reaction versus curing time, are plotted in Figure 4(a) for several temperatures. PMMA addition delayed the cure process, and a shoulder emerged in the reaction peak for temperatures $\geq 120^{\circ}$ C. On the other hand, in Figure 3, residual heat of quenched samples showed a shoulder when the precuring

Table II Glass Transition Temperatures for Quenched DGEBA-DDM-PMMA 1/1/15 Wt % Mixtures Cured at 80°C for Various Periods of Time

Curing Time (min)	T_g (°C)
120	$<\!\!40$
150	~ 40
180	75.9
210	85.7
285	95.0
330	97.4
375	96.9
420	97.5



Figure 3 dx/dT versus *T* for the unmodified DGE-BA–DDM 1/1 mixture (——) and for the DGEBA– DDM–15 wt % PMMA modified mixture (- - - -).



Figure 4 (a) Reaction rate versus time for the pure (——) and for the DGEBA-DDM-15 wt % PMMA modified mixture (---) at several cure temperatures. (b) Percentage of transmitted light versus time for the DGEBA-DDM-15 wt % PMMA modified mixture at several cure temperatures.

time was less than 150 min, denoting the phase separation process. Consequently, DSC measurements, alone or combined with other techniques, can be used for phase separation studies.

Light transmission is a common technique employed to analyze phase separation processes, as it allows one to detect particles with diameter $> 0.1 \ \mu\text{m}$. The results of TOM measurements are plotted in Figure 4(b) as the percentage of transmitted light versus curing time. Samples were also visually examined. For temperatures $\leq 120^{\circ}\text{C}$, a drop in the intensity of the transmitted light was not detected, and the samples were transparent, except the sample obtained a 120°C, which was translucent. For higher temperatures, the phase separation process was clearly observed, and the samples were opaque.

By comparing DSC isothermal thermograms with TOM measurements, it is possible to conclude that shoulders in the reaction peak are ascribed to the heat evolved in the phase separation process, so that the DSC technique is useful to monitor this phenomenon. Similar results were obtained by Fang et al.²¹ during the cure of an epoxy prepolymer with a cycloaliphatic diamine, modified with castor oil or with a carboxyl-terminated butadiene acrylonitrile rubber, showing that the heat evolved by the demixing process was between 3.7 and 4.6 J/g. The difference between the total heat of reaction for the PMMA modified system and the pure one is of the same order, that is, 3.05 J/g.

With the purpose of relating cloud-point times to conversion, a kinetic analysis was performed. Plots of the isothermal extent of reaction, as a function of time, for the neat and the 15-wt % PMMA-modified systems cured at various cure temperatures are shown in Figure 5. These curves were fitted assuming that the principal reactions are the addition of epoxy groups to primary and secondary amine hydrogens, respectively, and that both of them take place by two



Figure 5 The isothermal extent of reaction as a function of time for the pure (____) and for the DGEBA_DDM_15 wt % PMMA modified mixture (----) at several cure temperatures.

mechanisms, one uncatalyzed and the other catalyzed by the existing OH groups. The model proposed by Girard–Reydet et al.²² was used in this study:

$$\frac{dx}{dt} = \frac{(1-x)[\mathbf{K}' + \mathbf{K}F(\alpha)][2(1-r)\alpha + r\alpha^{r/2}]}{(2-r)}$$
$$\frac{d\alpha}{dt} = -2\alpha(1-x)[\mathbf{K}' + \mathbf{K}F(\alpha)]$$

where

$$F(\alpha) = 1 + \frac{(\mathrm{OH})_0}{e_0} - [(1-r)\alpha + \alpha^{r/2}]/(2-r)$$

and

$$\alpha = a_1/e_0$$
$$x = (e_0 - e)/e_0$$

In these expressions, e_0 and e are the concentration of epoxy equivalents at a time 0 and t, respectively; a_1 is the concentration of primary amino hydrogens, and r is the ratio of secondary to primary amino-hydrogen rate constants. The constants K and K' are the kinetic constants for the catalyzed and uncatalyzed reactions, respectively; $(OH)_0$ is the initial concentration of hydroxyl groups. At the beginning of the reaction, there are 0.15 eq OH/eq epoxy, coming from the

Table III Catalytic Constants for Pure $(K_{\rm p})$ and Modified System $(K_{\rm m})$ and the Noncatalytic Ones, $K'_{\rm p}$ and $K'_{\rm m}$

<i>T</i> (°C)	$\underset{(\min^{-1})}{K_{p}}$	$\substack{K_{\rm p}'\\(min^{-1})}$	$\mathop{K_{m}}\limits_{(min^{-1})}$	$\substack{K'_{m}\\(min^{-1})}$
80 100 120 140 200	0.01582 0.13806 0.25423 0.65900 5.40898	$0.00096 \\ 0 \\ 0.00347 \\ 0.00519 \\ 0.12760$	0.03497 0.05244 0.17030 0.47710 4.07630	$\begin{array}{c} 0.00046\\ 0.00307\\ 0.00403\\ 0.01494\\ 0.12009 \end{array}$

structure of the DGEBA molecule; and, thereafter, they are produced by addition reactions. It was assumed that the ratio of reactivities r between secondary and primary amino hydrogen is constant and equal to 0.65, as determined by Girard–Reydet et al.²²

Results obtained at different cure temperatures are shown in Table III. K_p and K_m are the catalytic constants for pure and modified systems, and K'_p and K'_m the noncatalytic ones. The preexponential factors and activation energies of Arrhenius expressions for kinetic constants are shown in Table IV. For both catalyzed and uncatalyzed mechanisms, within the experimental error, the activation energies corresponding to primary and secondary amine reactions were higher for the modified mixture than for the unmodified one. This fact seems to indicate that, although it is not usually considered, besides the dilution effect because of PMMA addition, other factors such as physicochemical interactions between components of the matrix formulation and the modifier used should be considered in order to better understand the relationships existing through curing between phase separation and reaction kinetics for thermosets modified with other polymers and oligomers.

Figure 6 shows cloud-point conversions obtained from kinetic curves of Figure 5 for the

Table IVPreexponential Factor A andActivation Energy E_a of Arrhenius Expressionsfor Kinetic Constants

Constant	$A (\min^{-1})$	E_a (kJ/mol)	
K _p K'p	$3.151 \ 10^6 \ 5.054 \ 10^6 \ 1.100 \ 1000\ \ 1000\ \ 1000\ \ 1000\ \ 1000\ \$	52.6 55.5	
K _m K' _m	$\frac{1.196}{8.999} \frac{10^{5}}{10^{5}}$	55.9 62.0	



Figure 6 Cloud point conversions obtained from kinetic curves at several isothermal temperatures. The asterisk represents the value obtained from a dynamic scan.

corresponding time of cloud-point, defined as the point where the shoulder emerges in isothermal and dynamic thermograms. The extrapolated value for the cloud-point conversion at 80° C is 0.68. Matêjka and Dusek²³ determined a gelpoint conversion equal to 0.62 for this neat system from critical mass relations experiments. This implies that, as gelation takes place, the modified system could not phase-separate at 80°C. From kinetic experiences, the measured gel time is 128.8 min. This result agrees with the fact that quenched samples will be phase-separated at 140°C if the precured time is shorter than 150 min.

Thus, the apparent miscibility shown by the mixtures precured for times longer than 3 h at 80°C could be a consequence of phase separation not occurring before gelation. Nevertheless, the existence of very small particles, appearing slightly before or after gelation, with diameter lower than the wavelength of visible light, could also explain the transparency of these mixtures. This possibility has been investigated in the second part of this study.

CONCLUSIONS

Phase separation and thermal behavior of 15 wt % PMMA epoxy mixtures precured at several temperatures have been investigated. The results obtained outline the importance of control

of the precuring conditions in order to obtain materials with several levels of miscibility with the same composition by only changing the precuring conditions. Thus, fully transparent mixtures can be obtained using long times at low precuring temperature, whereas opaque mixtures are obtained at short precuring times because gelation hindered the complete phase separation.

The phase-separation process, which occurs near the gelation of the matrix, can be monitored by calorimetric measurements, as a shoulder emerged in the calorimetric scans at times that correlate well with the cloud point time measured by optical microscopy.

For these autocatalytically reacting mixtures, thermoplastic incorporation leads to an increase of the activation energies for both catalytic and noncatalytic terms in the proposed model.

The importance of the final morphology on the ultimate properties, especially on the toughness of the epoxy matrix, will be reported in a future article.

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