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Poly(methyl methacrylate)-modified epoxy/amine system for reactive rotational moulding: crosslinking kinetics and rheological properties

Eskandar Mounif,[a] Genhai G Liang,[b] Wayne D Cook,[b]* Veronique Bellenger[a] and Aabbas Tcharkhatchi[a]

Abstract

BACKGROUND: The rotational moulding of thermosetting resins is hampered by their low viscosity and the abrupt increase in their viscosity as they polymerize. This study investigates the use of poly(methylmethacrylate) (PMMA) as a rheological processing aid in reactive blends of an aromatic diepoxy resin (diglycidyl ether of bisphenol-A, DGEBA) and an aromatic diamine (diethyltoluenediamine, DETDA) by studying the miscibility, curing, rheology, dynamic properties and morphology of the uncured solutions and of the resulting highly crosslinked polymer blends.

RESULTS: The PMMA was miscible in the uncured resins as expected from consideration of their solubility parameters, and the effect of PMMA concentration on the glass transition temperature, measured via differential scanning calorimetry (DSC), was fitted to several models. Addition of PMMA significantly increased the viscosity of the uncured blend which obeyed the log-additivity rule. The curing behaviour was monitored using DSC, infrared spectroscopy and dynamic rheology and it was found that addition of PMMA caused a small reduction in rate due to a dilution effect. The dynamic and steady shear rheologies were used to determine the gel point and gel relaxation index. Dynamic mechanical thermal analysis provided evidence for phase separation of the components into PMMA-rich domains and an epoxy-rich matrix and this was confirmed with electron microscopy studies.

CONCLUSION: These results indicate that addition of small amounts of PMMA to DGEBA/DETDA enlarges the processing window with regards to the rotational moulding of thermosets. In addition, the blending of small amounts (*ca* 10 wt%) of PMMA with the DGEBA/DETDA resin appears to cause only a modest sacrifice in thermal resistance.

Keywords: DETDA/DGEBA; epoxy/amine resin; chemorheology; thermoplastic-modified reactive system; phase separation; reactive rotational moulding

INTRODUCTION

Rotational moulding is the process of creating medium-to-large hollow products such as water and chemical storage tanks, bins and refuse containers, toys and playground equipment, automotive and aircraft components, helmets and kayak hulls, and often utilizes thermosetting resins whose cure is consistent with the relatively long cycle times (typically 20 min) and high temperatures employed in the process. Crosslinking epoxy/amine resins have been used in rotational moulding,[1] with the variation in their flow behaviour mainly being controlled by the increase of viscosity due to the increase in molecular weight during the branching stage of the crosslinking reaction. In the liquid rotational moulding process, we can distinguish two main stages of variation in the viscosity. The initial stage of the reaction is characterized by the formation of linear and branched oligomers. Due to the short branching, no chain entanglements exist and the viscosity is low compared to the weight equivalent of linear chain.[2,3] The second stage occurs when there is large-scale branching and the viscosity increases sharply followed by gelation due to the formation of an infinite macromolecule. Rotational moulding must be finished before this stage because no flow is possible after this critical point. Typical changes in the viscosity of a thermosetting resin during rotational moulding[1] are shown in Fig. 1. Due to the heat either applied to the mould or as a result of exothermic reaction, the viscosity usually drops initially as a result of the temperature rise. As noted above, the viscosity then slowly rises until the gel stage is approached, at which point this viscosity diverges to infinity.

The typical chemorheology of a reactive liquid system shown in Fig. 1 is not the ideal behaviour for rotational moulding. In liquid

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* *Correspondence to: Wayne D Cook, Department of Materials Engineering, Monash University, Wellington Road, Victoria 3800, Australia.*
E-mail: wayne.cook@eng.monash.edu.au

[a] *Laboratoire d'Ingénierie des Matériaux (LIM), Ecole Nationale Supérieure d'Arts et Métiers (ENSAM), 151 boulevard de l'Hôpital, 75013 Paris, France*

[b] *Department of Materials Engineering, Monash University, Wellington Road, Victoria 3800, Australia*

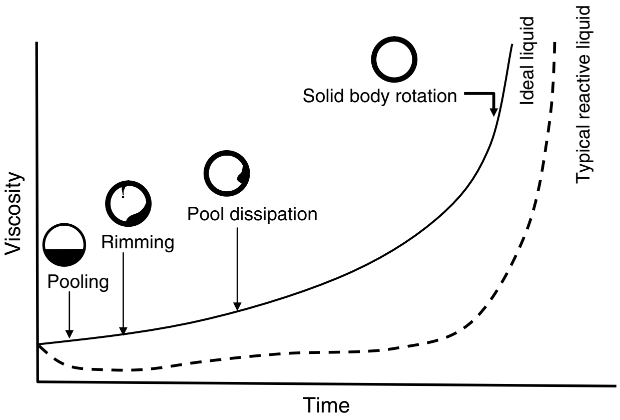

Figure 1. Typical variation of viscosity with curing time for a reactive liquid compared with ideal flow behaviour. (Redrawn from Figure 6.39 of Crawford and Throne[1] with modification).

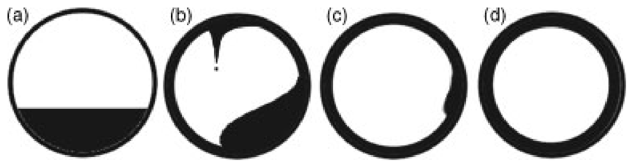

Figure 2. Typical steps of liquid rotational moulding: (a) rotating pool; (b) cascading flow; (c) rimming; (d) solid body rotation.

rotational moulding there are four main steps, as shown in Fig. 2. For each regime a certain viscosity is required. At the start of the process, the viscosity needs to be relatively low so that the rotating pool mixes the ingredients and only deposits a thin film of reactive resin on the mould surface. As the processing time progresses, the viscosity should slowly rise so that the cascading flow distributes a thicker layer evenly over the mould. In the last flow phase, rimming finalizes the even distribution of resin on the mould until gelation approaches, resulting in the solid body rotation step. If there is insufficient time for each of these steps then poor mixing of reacting components will occur and an uneven part thickness will result. For example, as can be seen in Fig. 1, the typical increase of viscosity during crosslinking is often not high enough and the dominant regime is that of the rotating pool.

It does not appear to be widely understood that this problem in flow behaviour could potentially be solved by adding a soluble thermoplastic polymer to the reactive system, so that the viscosity can be increased during the pre-gel phase where only low molecular weight epoxy/amine oligomers are formed and allow each of the flow stages to develop smoothly. At the same time, the addition of the thermoplastic could improve the mechanical properties of the finished part, such as enhanced toughness[4] or reduced shrinkage.[5]

Poly(methylmethacrylate) (PMMA) has many applications as an additive, one of them being its use to control the temperature-dependent viscosity of lubricating oils and hydraulic fluids.[6] PMMA also shows a very good solubility with uncured epoxy resins.[7] The epoxy/amine–PMMA system has been the subject of many recent research works[7–16] as a model for the toughening of thermosets by small amounts of thermoplastics which phase-separate during cure. However, the properties of cured epoxy–PMMA blends depend on the curing agent used: some workers[7,17–19] have observed phase separation during cure with particular curatives whereas other curatives did not appear to cause phase separation.[7,20]

The selected reactive system investigated in the present work consisted of the diglycidyl ether of bisphenol-A (DGEBA) and an aromatic diamine, diethyltoluenediamine (DETDA), whose kinetics have been studied in previous work.[21] This diamine is of interest because it reacts with DGEBA to form a highly crosslinked epoxy thermoset with a very high glass transition temperature. The miscibility of PMMA in DGEBA and in DGEBA/DETDA and the effect of the PMMA content on the viscosity of the uncured system were investigated. The curing kinetics of these blends were monitored and compared with their chemorheology. The effect of PMMA on the thermomechanical properties and morphology of the blends was then determined.

EXPERIMENTAL

Materials

The curing system studied was DGEBA with an equivalent weight of 171 g mol^{-1} (DER332, from Dow) cured with the primary amine DETDA (from Safic Alcan). PMMA powder (from ARKEMA) with a molecular weight of 50 000 g mol^{-1} was used as the viscosity modifier. Figure 3 shows the structures of the materials used.

All blends were first prepared by mixing PMMA and DGEBA. For systems containing up to 25.4 wt% PMMA, the DGEBA and PMMA were mixed and heated to 140 °C under continuous stirring until a transparent liquid was obtained. For PMMA/DGEBA blends containing more than 25.4 wt% PMMA, the components were premixed at room temperature and then extruded at 200 °C with a MiniLab micro-extruder (Haake, Thermo Electron, Germany). The formation of a single liquid phase was verified by the observation of a single glass transition using DSC. For curing systems, a stoichiometric amount of DETDA (20.4 wt% DETDA to 79.6 wt% DGEBA) was added to and mixed with the PMMA/DGEBA blend at room temperature. These samples are identified by a code that describes the percentage by weight of PMMA in the mixture so that the system 16.6% PMMA/DGEBA/DETDA refers to a reactive blend containing 16.6 wt% PMMA in the whole blend that was prepared from 20 parts of PMMA to 80 parts of DGEBA plus the stoichiometric level of DETDA.

DSC analysis

DSC was used to measure the glass transition temperatures of the resins with a scanning rate of 10 °C min^{-1} using a Perkin Elmer Pyris 1 fitted with a Flexicool (ETS system) cooling system. The curing behaviour was also measured during this temperature ramping experiment.

Near-infrared spectroscopy

The kinetics of crosslinking was studied *in situ* by measuring the absorbance[22] of the primary amine at 5063 cm^{-1} and epoxy at 4529 cm^{-1} with a Perkin Elmer Spectrum GX spectrophotometer using glass microscope slide windows separated by a 1 mm rubber gasket to allow for shrinkage during the curing reaction. The phenyl C–H absorption peak at 4676 cm^{-1} was used as reference peak[22] to determine the conversion of the chemical groups:

$$x = 1 - \frac{A_t/A_t^{\mathrm{ref}}}{A_0/A_0^{\mathrm{ref}}} \tag{1}$$

where A_t is the absorbance of the reacting species at time t and $A_t{}^{\mathrm{ref}}$ is the absorbance of the reference peak at time t.

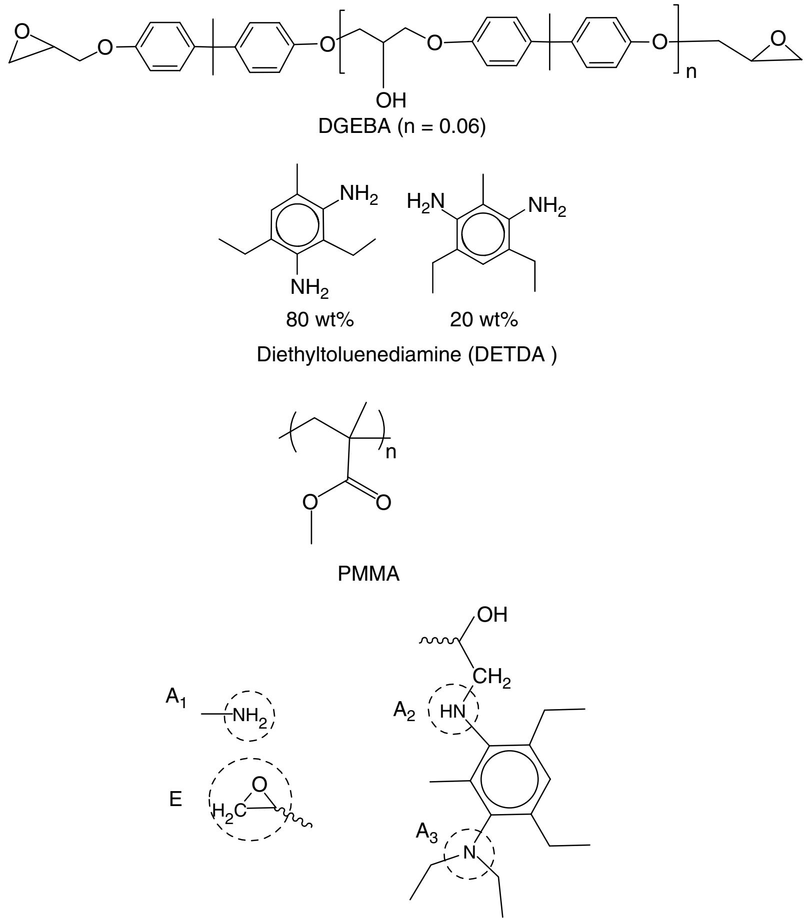

Figure 3. Chemical structures of materials used and the notation used to identify the reacting chemical groups.

Rheological analysis

The dynamic viscosity and moduli were measured with an ARES rheometer (Rheometric Scientific, USA) using parallel plates of 40 mm diameter and a plate gap of 0.5–1 mm at oscillation frequencies ranging from 0.1 to 10 Hz. To maximize the dynamic measurement range during these experiments, the strain was automatically varied using the Orchestrator software from 100% for a modulus of less than 10^2 Pa to 0.1% for a storage modulus greater than 10^7 Pa. The gel point was determined using the Chambon–Winter criterion[23] of a frequency independence of tan δ. Steady shear viscosity was measured with a Physica rheometer at a shear rate of $0.1\ \text{s}^{-1}$ using parallel plates of 40 mm diameter and a plate gap of 0.5–1 mm.

Dynamic mechanical thermal analysis (DMTA)

The PMMA/DGEBA/DETDA samples for DMTA were cured at 160 °C for 11 h, then post-cured at 220 °C for 1 h. Mechanical spectroscopy was carried out with a Mark IV DMTA instrument (Rheometric Scientific, USA) with parallelepiped specimens (2.5 mm ×6 mm ×35 mm) tested at 1 Hz in dual cantilever mode using a heating rate of $2\ ^\circ\text{C min}^{-1}$ from room temperature up to 250 °C.

SEM analysis

SEM images were obtained with a JEOL JSM-6300F instrument operating at 15 kV. The cured blend specimens were fractured in liquid nitrogen, and the fracture surface was gold-sputtered either with or without etching in acetone for 3 min with stirring.

RESULTS AND DISCUSSION

Initial solubility

The solubility of PMMA in DGEBA is well known[24] and is enhanced by the hydrogen bonding interaction between the PMMA carbonyl groups and the hydroxyl groups of the DGEBA oligomer. A Fourier transform mid-infrared study of the cure of DGEBA with an aliphatic diamine in the presence of 2 wt% PMMA also demonstrated[8] that hydrogen bonding occurs between the PMMA carbonyl and the hydroxyl groups formed during the curing of DGEBA with diamines. For the present system, we can also obtain an indication of the level of miscibility by comparing the solubility parameters of PMMA, DETDA and DGEBA, as listed in Table 1. Since a mixture with a solubility parameter difference of less than 2 is considered to be miscible,[25] PMMA/DGEBA/DETDA should be a soluble mixture.

Glass transition temperature *versus* weight fraction of PMMA in blends

To verify that the mixing procedure was efficient and the DGEBA/PMMA binary system formed a homogeneous solution, DSC was used to confirm that there was a single glass transition temperature T_g. In the case of miscible binary blends, T_g can be

Table 1. Solubility parameters ($J^{1/2}$ $cm^{-3/2}$) for the components as calculated by group contribution to cohesive energy densities[26]

Material	Solubility parameter[26]	Solubility parameter (literature values)
DGEBA	22.5	23.1[27]
DETDA	22.1	19.9[a]
PMMA	20.9	22.7;[27] 23.1[28]

[a] http://www.wikipatents.com/ca/2215479.html (DETDA: 9.73 cal$^{1/2}$ cm$^{3/2}$).

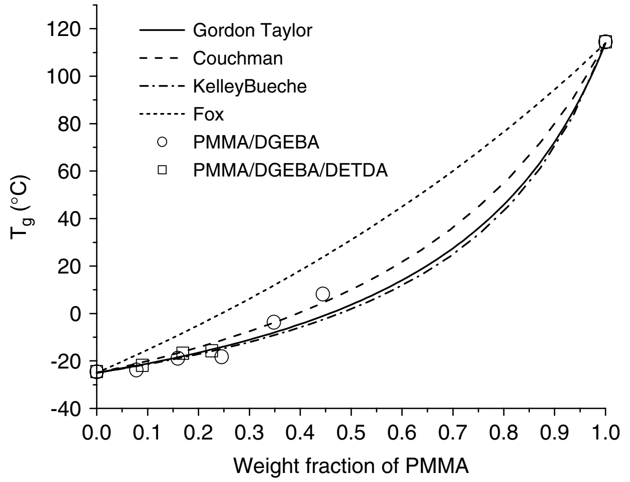

Figure 4. Variation of the glass transition temperature of the PMMA/DGEBA blends and the reactive PMMA/DGEBA/DETDA blends compared to literature equations.[29–32].

predicted by the following Kelley–Bueche,[29] Couchman,[30] Fox[31] and Gordon–Taylor[32] equations, respectively:

$$T_g = \frac{v_1 \alpha_{p1} T_{g1} + v_2 \alpha_{p2} T_{g2}}{v_1 \alpha_{p1} + v_2 \alpha_{p2}} \tag{2}$$

$$\ln(T_g) = \frac{w_1 \Delta C_{p1} \ln(T_{g1}) + w_2 \Delta C_{p2} \ln(T_{g2})}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{3}$$

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{4}$$

$$T_g = \frac{w_1 T_{g1} + \kappa w_2 T_{g2}}{w_1 + \kappa w_2} \tag{5}$$

where T_g and T_{gi} ($i = 1, 2$) are the glass transition temperatures of the blend and component i, ΔC_{pi} is the heat capacity change at T_g, w_i is the weight fraction of component i, v_i is the volume fraction of component i and α_i is the thermal expansion coefficient. Figure 4 shows that the Gordon–Taylor and Couchman equations fit the experimental points best with the parameter κ equal to 0.26, which is equal to the ratio $\Delta C_{p2}/\Delta C_{p1}$, as measured by DSC. This agreement supports the miscibility and homogeneity of the uncured blend. Gomez and Bucknall[18] also fitted T_g for DGEBA/PMMA blends using the Gordon–Taylor equation using a similar value of the parameter κ.

Steady shear viscosity

Figure 5 shows the variation in steady shear viscosity *versus* the PMMA weight fraction at 140 °C. The logarithm of initial viscosity

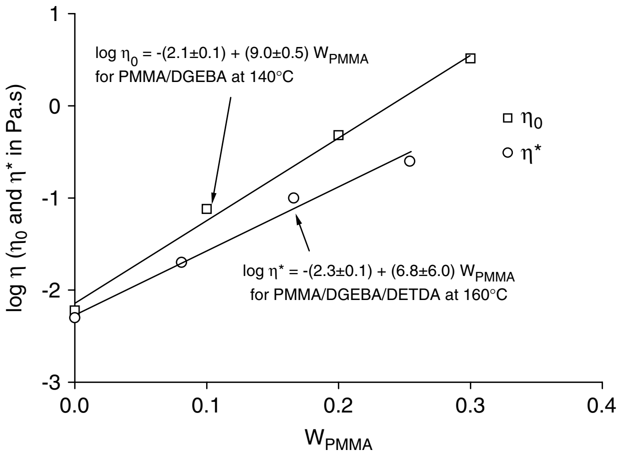

Figure 5. Isothermal steady shear viscosity (at 140 °C) measured at 1 s^{-1} shear rate *versus* weight fraction of PMMA for the PMMA/DGEBA binary system and the complex shear viscosity (at 160 °C) measured at 1 Hz for the reactive PMMA/DGEBA/DETDA tertiary blend.

is well described by the log-additivity rule:

$$\log \eta = w_{\mathrm{PMMA}} \log \eta_{\mathrm{PMMA}} + (1 - w_{\mathrm{PMMA}}) \log \eta_{\mathrm{DGEBA/DETDA}} \tag{6}$$

where η, η_{PMMA} and $\eta_{\mathrm{DGEBA/DETDA}}$ are the viscosities (Pa s) of the blend, the PMMA and the DGEBA or DGEBA (or DGEBA/DETDA) resin, respectively, and w_{PMMA} is the weight fraction of PMMA in the blend. This equation is predicted from free volume considerations[33] and observed in a number of polymer-reactive diluent studies.[34]

Kinetics of cure

Figure 6 shows the curing behaviour of the blends as determined using dynamic DSC. The onset and peak temperatures increase slightly as the concentration of PMMA increases, indicating that the rate of reaction is reduced. This is consistent with a concentration dilution effect in which the presence of the non-reacting PMMA dissolved in the blend dilutes the reacting epoxy and amine groups. The heat of polymerization of DGEBA/DETDA is found to be approximately 74 kJ mol^{-1} which is lower than the value of 100 kJ mol^{-1} usually found for epoxy/amine systems.[35] This is

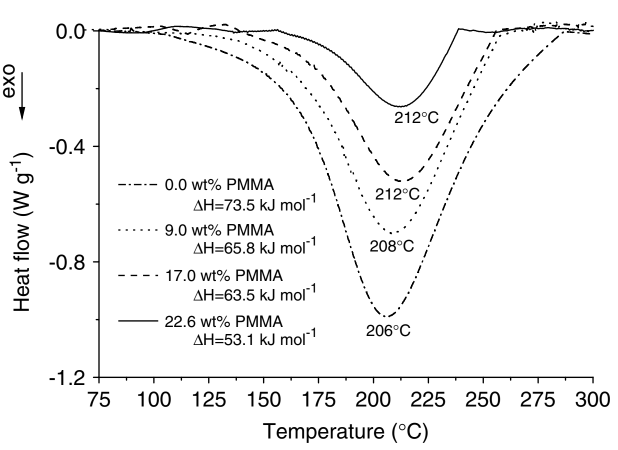

Figure 6. Temperature ramping (10 °C min^{-1}) DSC curves for the cure of PMMA/DGEBA/DETDA blends.

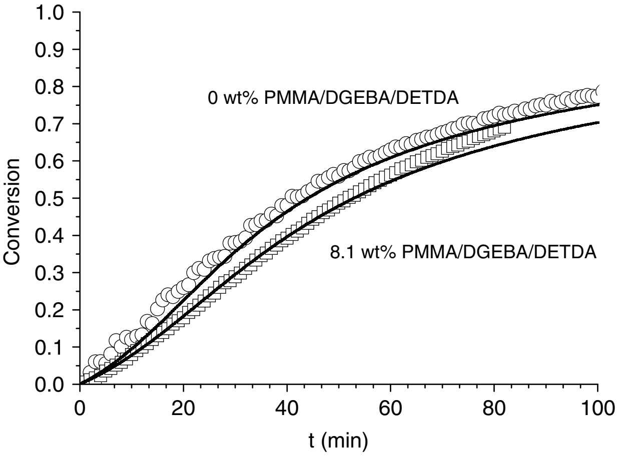

Figure 7. Conversion of epoxy groups during crosslinking at 140 °C for the two systems indicated. The solid curves were calculated from Eqns (7)–(10) as explained in the text.

probably a result of the high curing temperature required for this system which leads to some degradation in the material during cure and a reduction in the heat of polymerization. The heat of polymerization also is reduced systematically as the concentration of PMMA in the blend increases which may be a topological effect[36] in which the PMMA segments spatially restrict some of the amine and epoxy groups from approaching one another, thus reducing the degree of cure.

Based on an autocatalytic mechanism[37] for cure without etherification or impurity catalysis, the following differential equations can be used to predict the concentration of reactive groups during the polymerization reaction:

$$\frac{\mathrm{d}[\mathrm{E}]}{\mathrm{d}t} = -k_1[\mathrm{A}_1][\mathrm{E}] - k_2[\mathrm{A}_2][\mathrm{E}] - k_{1\mathrm{c}}[\mathrm{A}_1][\mathrm{E}][\mathrm{OH}] - k_{2\mathrm{c}}[\mathrm{A}_2][\mathrm{E}][\mathrm{OH}] \tag{7}$$

$$\frac{\mathrm{d}[\mathrm{A}_1]}{\mathrm{d}t} = -k_1[\mathrm{A}_1][\mathrm{E}] - k_{1\mathrm{c}}[\mathrm{A}_1][\mathrm{E}][\mathrm{OH}] \tag{8}$$

where [E] is the concentration of epoxy groups, [OH] is the concentration of hydroxyl groups either present initially (see the structure of the DGEBA oligomer in Fig. 3) or formed during the reaction and $[\mathrm{A}_1]$ and $[\mathrm{A}_2]$ are the concentrations of primary and secondary amines. In addition, the equations for the conservation of mass can be written as[22]

$$[\mathrm{OH}] = [\mathrm{OH}]_0 + [\mathrm{E}]_0 - [\mathrm{E}] \tag{9}$$

$$[\mathrm{A}_2] = 2([\mathrm{A}_1]_0 - [\mathrm{A}_1]) - ([\mathrm{E}]_0 - [\mathrm{E}]) \tag{10}$$

Bonnet *et al.*[38] found that the rate of epoxy conversion in a blend of an epoxy/amine system with low levels of a thermoplastic was reduced in comparison to the neat system due to a dilutional effect, but for higher concentrations of the thermoplastic (>30 wt% polyetherimide or polystyrene) the rate of the reaction abruptly increased when reaction-induced phase separation occurred. This transition was explained by the increase in concentration of reactive groups in the epoxy/amine-rich phase following phase separation. In the present work, only a dilution effect was observed for the kinetics of the 8.1 wt% PMMA/DGEBA/DEDTA system (Fig. 7). The conversion data were fitted to Eqns (7) and (8) using the Runge–Kutta method, assuming a reactivity ratio of 0.25, which has been determined previously.[21,22] A dilution factor of 0.902 was used to account for the difference in concentrations of epoxy groups due to the addition of PMMA. Both sets of epoxy conversion data shown in Fig. 7 were well fitted to the kinetic model.

Viscosity variation

Figure 8 shows the steady shear viscosity of the 8.1 wt% PMMA-modified system during crosslinking at 140 °C compared with the cure of the non-modified system. The addition of PMMA to the reactive resin not only increases the viscosity during the pre-gel phase but also makes the divergence of the viscosity less sharp, as indicated from the logarithmic plot in Fig. 8(a) and the rescaled data in the inset of Fig. 8(b). Similar behaviour has been observed for blends of reactive plasticizers with poly(vinyl chloride).[34] This change in the viscosity profile allows the rotational moulding to be more efficient because it allows for the various stages of flow to develop during cure as shown in Fig. 1. This behaviour can be partly explained by a consideration of the log-additivity rule for the viscosity of the reacting DGEBA/DETDA resin when PMMA is added (Eqn (6)). In this case the first term dominates the rheology in the initial reaction stages and the second term only becomes important when large-scale chain branching and crosslinking occur. However, this does not explain why the ratio of

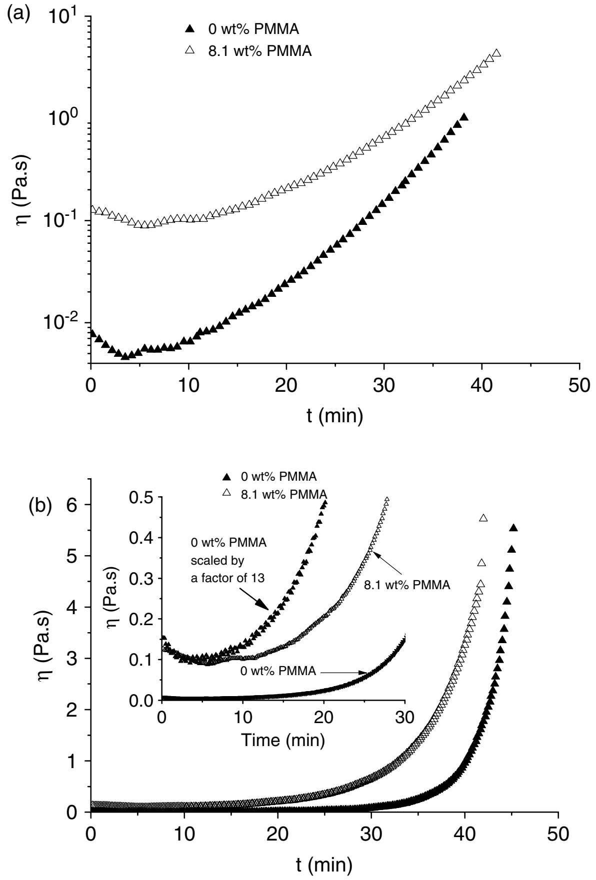

Figure 8. (a) Logarithm of steady shear viscosity at 140 °C measured at a shear rate of 1 s^{-1} during crosslinking of the 8.1 wt% PMMA/DGEBA/DETDA system compared to the non-modified system (0 wt% PMMA). (b) Linear plot of the steady shear viscosity data with an inset in which the data for 0 wt% PMMA have been rescaled to the same starting viscosity as the 8.1 wt% PMMA/DGEBA/DETDA system. For clarity, not all of the data points are plotted.

the viscosities of the two reacting systems becomes closer to unity (i.e. the differences in the logarithms of viscosity are reduced) in the latter stages of the reaction. Possibly this is caused by reaction-induced phase separation of the PMMA from the epoxy matrix into dispersed particles which would reduce the effect of the PMMA on the matrix viscosity – similar behaviour has been reported by Bonnet *et al.*[39] Fig. 9 shows the variation in dynamic viscosity of the blends during cure. As with the steady shear viscosity, the complex viscosity increases considerably on the addition of PMMA. It should be noted that the Cox–Merz[40] relationship which approximates the complex viscosity to the steady shear viscosity fails as the gel point is approached and this explains the large differences between the steady shear data (Fig. 8) and dynamic data (Fig. 9) as the gel point is approached.

The typical variation in loss factor at various frequencies *versus* curing time is shown in Fig. 10 for the blend with 16.6 wt% PMMA. Due to the low moduli of the resin in the early stages of the cure, tan δ does not show any systematic variation in frequency; however, after 25 min, the data show the characteristic behaviour of a viscoelastic liquid: a decrease in tan δ with increasing frequency. At 45 min tan δ becomes independent of frequency, which indicates the formation of a gel as defined by the Winter–Chambon criterion.[18]

Table 2 lists the gel time measured at 140 °C for each of the systems studied. The gel time is not affected significantly by the addition of PMMA, except for the highest level of PMMA (25.4 wt%) which may be explained by the greater dilution effect of PMMA on the curing of the network. The gelation relaxation exponent (n) calculated for the value of tan δ at the gel point[23] is the power law index of G' and G'' with frequency. These exponents are shown in Table 2 to decrease with increasing PMMA content, but the reason for this behaviour is unclear.

The dynamic rheology during cure was also measured as a function of temperature (Fig. 11). As expected, increasing temperature reduced viscosity and gelation time. Thus by varying the concentration of PMMA in the blend and the curing temperature, the rheological behaviour can be adjusted to suit the rotational moulding requirements. Assuming that the gel point conversion is independent of the cure temperature, the linear relations between the natural logarithm of gel point and the reciprocal of the absolute temperatures give the activation energies for polymerization listed in Table 2. Given the magnitude of the uncertainty, the activation energy appears to be independent of the PMMA concentration and the overall activation energy was determined to be 81 ± 14 kJ mol^{-1}, which is somewhat higher than the value of 60 kJ mol^{-1} determined previously for neat DGEBA/DETDA[21] and the range 60–70 kJ mol^{-1} for polyetherimide/DGEBA/DETDA.[41]

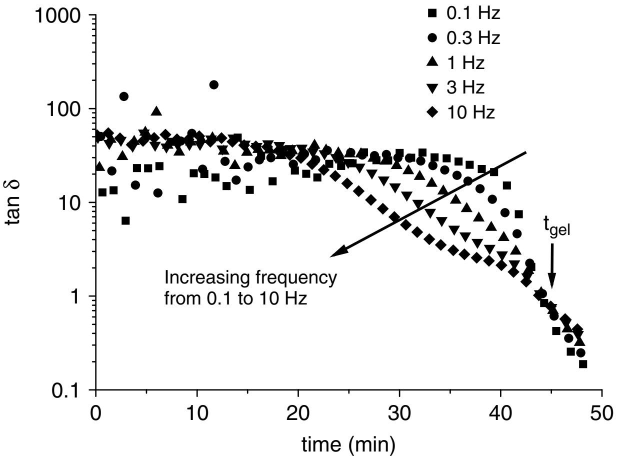

Figure 10. Loss factor *versus* curing time for 16.6 wt% PMMA/DGEBA/DETDA.

Table 2. Gel time of the PMMA/DGEBA/DETDA systems cured at 140 °C, gelation relaxation exponent (n) and the activation energy (E_a) of the gel point

PMMA (wt%)	0	8.1	16.6	25.4
Gel time (min)	46	44	45	56
n	0.71	0.55	0.45	0.36
E_a (kJ mol^{-1})	74 ± 19	88 ± 12	88 ± 12	75 ± 13

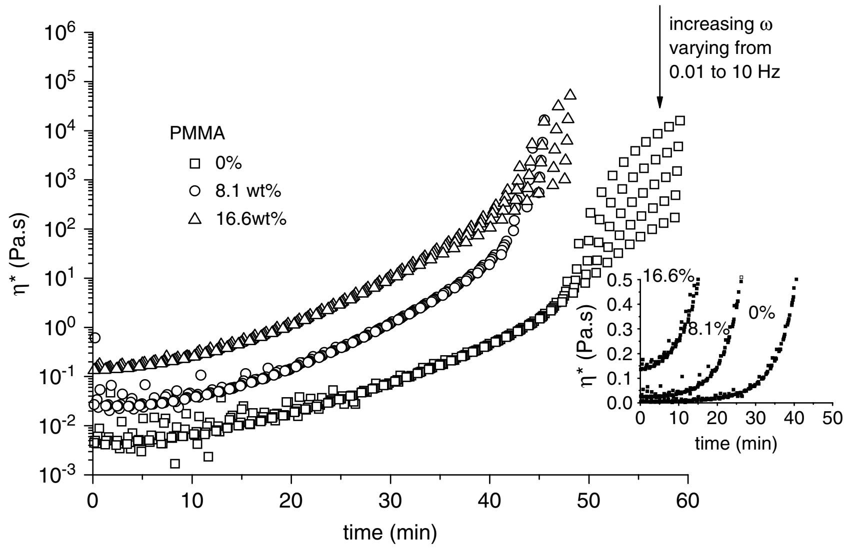

Figure 9. Complex dynamic viscosity at 140 °C *versus* curing time for PMMA/DGEBA/DETDA with varying amounts of PMMA.

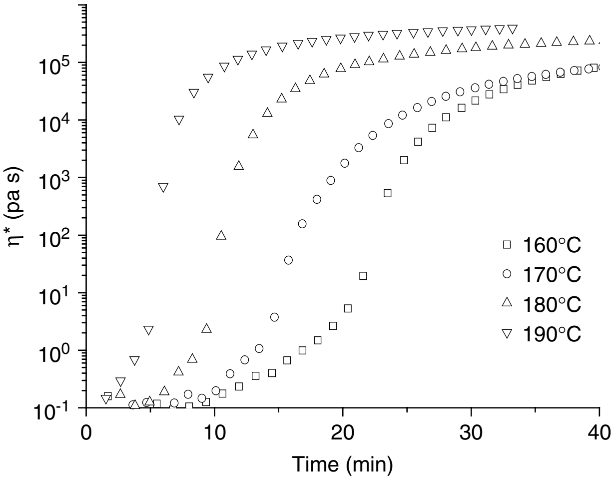

Figure 11. Complex dynamic viscosity at 1 Hz *versus* curing time for 8.8 wt% PMMA/DGEBA/DETDA at various temperatures.

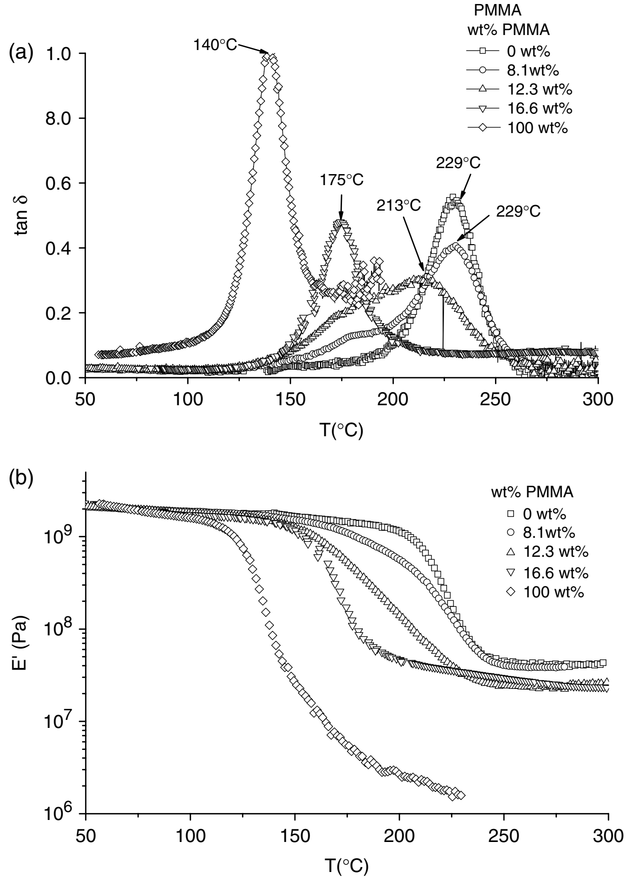

Figure 12. DMTA for PMMA/DGEBA/DETDA blends: (a) loss factor; (b) real flexural modulus. For clarity, some of the data points are not plotted.

DMTA measurements

The dynamic mechanical spectra of the PMMA/DGEBA/DETDA blends are shown in Fig. 12. Both DGEBA/DETDA and PMMA exhibit one main glass transition peak – the rise in tan δ at the highest temperatures for PMMA is due to viscous flow behaviour. In contrast, the blends show two transitions, indicating two phases. The 8.1 wt% PMMA/DGEBA/DETDA sample exhibits a major glass transition at the same temperature as the pure epoxy resin indicating that this phase is pure DGEBA/DETDA. This blend also has a shoulder on the low-temperature side of the main relaxation peak which corresponds most probably to the glass transition of a PMMA-rich phase. Since the peak temperature is well above that of pure PMMA, this second phase appears to contain epoxy resin also. For the 12.3 wt% PMMA/DGEBA/DETDA sample, the high-temperature peak is shifted to lower temperatures, suggesting that the epoxy matrix also contains some PMMA. The 16.6 wt% PMMA/DGEBA/DETDA sample only shows one transition which suggests that the two phases have similar composition. The overall behaviours shown here in the DMTA data are similar to the reaction-induced phase separation reported by Ritzenthaler *et al.*[7] for an epoxy/amine modified by PMMA, by Guo *et al.*[42] for an epoxy resin modified by a hyperbranched polyester and by Cook *et al.*[43] for unsaturated polyester and vinyl ester resins blended with poly(vinyl acetate).

The curves of the real dynamic flexural modulus (E') in the glass transition region for pure PMMA and pure DGEBA/DETDA are relatively sharp; however, the blends show broader relaxation behaviour which is consistent with the overlapping of transitions due to the PMMA-rich and epoxy-rich regions. The modulus after the glass transition of the specimens containing epoxy resin is very high (*ca* 30–50 MPa), due to the highly crosslinked matrix and confirms that for these blends the epoxy is a continuous phase. Using a glassy modulus of 1 GPa as an indicator of the stress-bearing capability of a material, E' drops to 1 GPa at 206 °C for DGEBA/DETDA, at 180 °C for 8.1 wt% PMMA/DEGDA/DETDA, at 160 °C for 12.3 wt% PMMA/DEGDA/DETDA and at 155 °C for 16.6 wt% PMMA/DEGDA/DETDA. This indicates that blending of PMMA with the epoxy resin causes a modest sacrifice in thermal resistance but this may be justified by an enhancement in other properties. For example, Galante *et al.*[19] observed that low concentrations of PMMA (5 wt%) can increase the fracture toughness of anhydride-cured epoxy.

Figure 13 shows SEM images of the fracture surfaces of the 16.6 wt% PMMA/DEGDA/DETDA blend. For the non-etched surface (Fig. 13(a)), 0.1 μm particles can be observed projecting from the surface; for the etched surface (Fig. 13(b)), these particles are replaced by similar sized depressions. This confirms that the particles are PMMA.

CONCLUSIONS

The effect of addition of PMMA on the cure behaviour and properties of highly crosslinked DGEBA/DETDA was investigated. A single glass transition was observed in the uncured blends, confirming miscibility, and T_g was raised by the addition of PMMA in accord with the Gordon–Taylor and Couchman equations. The viscosity of the uncured blends was significantly increased on addition of PMMA to either DGEBA or the stoichiometric DGEBA/DETDA blend and the logarithmic additivity rule for viscosity was obeyed.

The cure kinetics were monitored using DSC and infrared spectroscopy and the dilution effect of PMMA on the kinetics was observed. The rheology during cure was studied and a significant improvement of the viscosity–time profile was observed which suggests that rotational moulding of thermosets can benefit from thermoplastic modification. The gel time was not significantly altered on increasing the PMMA content; however, the power-law index decreased. The activation energy for gelation was relatively independent of the PMMA level. Thus the rheological requirements of a specific rotational moulding operation, such as gel

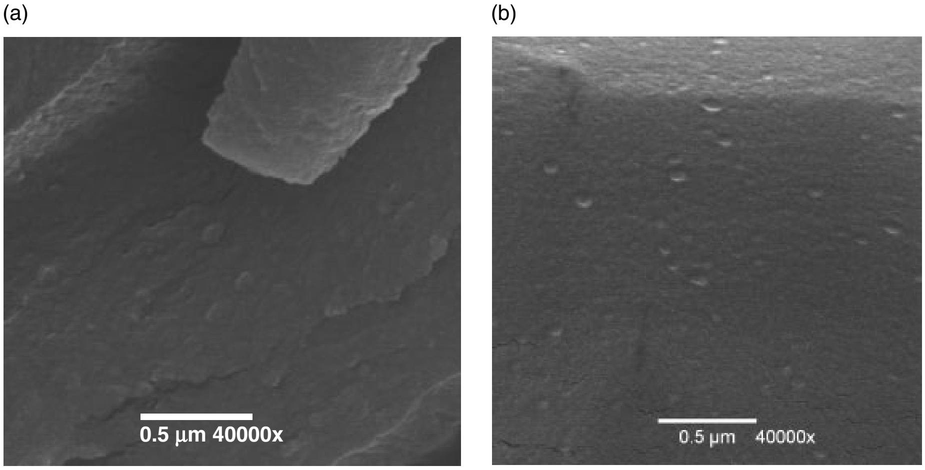

Figure 13. SEM images of (a) non-etched and (b) etched freeze-fractured surfaces of 16.6 wt% PMMA/DEGDA/DETDA.

time and initial viscosity, can be obtained by adjusting the cure temperature and the concentration of PMMA.

DMTA studies of the cured samples revealed two transition regions in the viscoelastic spectrum providing evidence of phase separation of a PMMA-rich dispersed phase in the thermoset matrix. SEM studies confirmed the presence of PMMA-rich nanoparticles embedded in the epoxy matrix.

Thus it appears that the addition of small amounts of PMMA to DGEBA/DETDA specifically, and by inference of thermoplastics to thermosetting resins generally, enlarges the processing window with regards to the rotational moulding of thermosets. In addition, the blending of small amounts (*ca* 10 wt%) of PMMA with the DGEBA/DETDA resin appears to cause only a modest sacrifice in thermal resistance even for high-T_g matrices such as that used here.

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