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# Influence of epoxy hardener on miscibility of blends of poly(methyl methacrylate) and epoxy networks

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## Abstract

In this paper, we investigate poly(methyl methacrylate) (PMMA)-modified epoxy thermoset based on DGEBA before and after curing of the epoxy with various aromatic amines by means of different techniques: Differential Scanning Calorimetry (DSC), Size Exclusion Chromatography (SEC), Infra-Red Spectroscopy (FT-IR), Dynamic Mechanical Analysis (DMA) and Transmission Electron Microscopy (TEM). The DSC analyses demonstrate the complete miscibility between PMMA and DGEBA. Neither specific interaction nor trans-esterification reaction is revealed by SEC and FT-IR between these components. With respect to reactive blends, the nature of the curing agent affects the polymerization kinetics and the structure of the PMMA-modified epoxy network. The usual polymerization induced phase separation occurs using DDS or MDA leading to a material with a two-phase structure revealed by TEM and DMA. On the other hand, the use of MCDEA as curing agent does not entail any noticeable phase separation during curing even if cured samples appear slightly turbid. No acceleration of the epoxy–amine reaction can be observed contrary to DDS and MDA based blends presenting the usual acceleration of the reaction just after the phase separation. In the case of blends using MCDEA as the hardener, we really have what some call a semi-IPN.

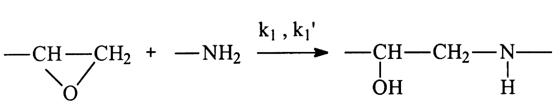
*Keywords*: Poly(methyl methacrylate); Epoxy resin; Miscibility

## 1. Introduction

Thermoplastic–epoxy systems have been widely studied in the past 20 years in the literature. The aim is to increase the toughness of epoxy thermoset with a thermoplastic rich phase [1,2] or to improve processing techniques for high temperature resistant thermoplastic polymers [3,4].

Most of the studies reported deal with an initial homogeneous mixture consisting of a thermoplastic that dissolves in an epoxy precursor: the epoxy monomer and its curing agent. Indeed, diglycidyl ether of bisphenol A (DGEBA) is a solvent for many linear polymers such as polyetherimide (PEI) [1,5–7], poly(2,6-dimethyl-1,4-phenylene) ether (PPE) [3,4], poly(ether sulfone) (PES) [8,9] and poly(methyl methacrylate) (PMMA) [10–13]. During the curing process of thermoset precursors, the molar mass increase involves a decrease in the conformational entropy of mixing and the phase separation between the thermoplastic and the forming epoxy polymer occurs. This polymerization-induced phase separation greatly depends on the initial composition of the blend, that is to say the mass fraction of thermoplastic $\Phi^0_{TP}$ according to the critical composition $\Phi_{TP,crit}$, [6]. Phase separation process may occur by spinodal demixing (SD) for thermoplastic concentration near $\Phi_{TP,crit}$, or by a nucleation growth (NG) mechanism for off-critical composition. In that way, various morphologies can be observed: a bicontinuous structure near $\Phi_{TP,crit}$, but a thermoset or thermoplastic rich continuous phase for thermoplastic concentrations, respectively, lower or higher than $\Phi_{TP,crit}$. Initial miscibility, polymerization rate and, eventually, reaction between thermoplastic and epoxy are also important factors that control the final structure of the material.

The diamine–epoxy reaction can be described as follows:



(1)

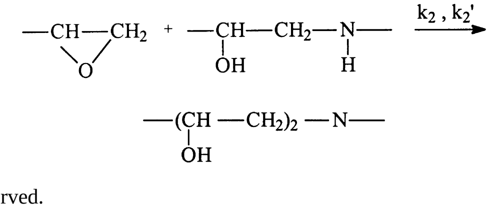


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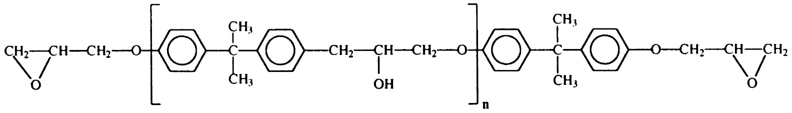
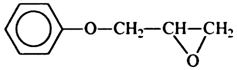
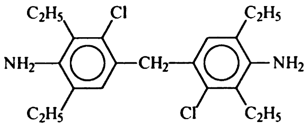
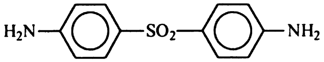
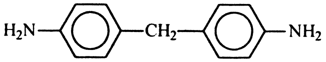
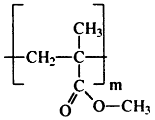
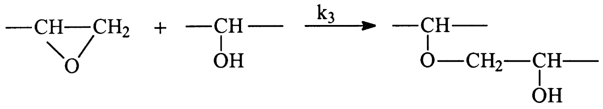
Table 1
Characteristics of components used

| Name | Designation | Chemical structure | Molar mass (g mol$^{-1}$) | Supplier |
|---|---|---|---|---|
| Diglycidyl ether of bisphenol A | DGEBA |  | 382.6 $\bar{n} = 0.15$ | Ciba Geigy |
| Phenyl glycidyl ether | PGE |  | 150 | Aldrich |
| 4,4′-methylenebis-[3−chloro2,6diethylaniline] | MCDEA |  | 380 | Lonza |
| 4,4′-diaminodiphenyl sulfone | DDS |  | 248 | Fluka |
| 4,4′-methylene dianiline | MDA |  | 198 | Aldrich |
| Polymethyl methacrylate | PMMA |  | 47 000 ($\bar{M}_n$) | Elf Atochem |



(3)

Reaction (1) presents the addition reaction of primary amine hydrogen with epoxy group. Then the secondary amine formed reacts with another epoxy group to create a tertiary amine (Reaction (2)). The reactions are known to be auto-catalyzed by OH groups formed during the process. $k_1$ and $k_2$ are the rate constants of the catalyzed reactions between epoxy and primary and secondary amine, respectively, whereas $k'_1$ and $k'_2$ are the corresponding rate constants of the non-catalytic reactions.

Reaction (3) presents the etherification reaction between epoxy functions and hydroxyl groups. Most of time, this reaction is neglected. In our case, infrared analysis during curing have shown that it occurred actually in the case of one diamine, 4,4′-methylenebis[3–chloro2,6–diethylaniline] (MCDEA) but not in the case of the two others diamines, 4,4′-diaminodiphenyl sulfone (DDS) and 4,4′-methylene dianiline (MDA) [14].

The addition of a non-reactive thermoplastic leads to a dilution effect of reactive groups and, therefore, to a decrease of the epoxy amine reaction rate. Besides, if a polymerization induced phase separation occurs during cure, an increase in the reaction rate can be observed for high thermoplastic concentration ($\Phi^0_{\mathrm{TP}} > 30$ wt%), owing to the existence of an epoxy–amine rich phase with higher concentration of reactive groups. Bonnet et al. [7] have observed and modeled this phenomenon for two thermoplastics, polystyrene (PS) and PEI in a DGEBA / MCDEA thermoset system.

With regards to PMMA as the thermoplastic, one important fact is that an initial homogeneous solution with DGEBA was obtained over the entire composition range [11,12]: a single glass transition temperature characterized all the solutions containing PMMA.

Some authors [12] also studied the possible physical interactions (hydrogen bonding) between PMMA and DGEBA. In the case of DGEBA/PMMA blends (PMMA content 33.3 wt%) heated at 220°C, they did not notice any modification of the C=O absorption peak. Conversely, Janarthanan and Thyagarajan [13], who studied similar blends at room temperature with various thermoplastic concentrations, observed and attributed the modification of this peak to hydrogen bonding between the C=O groups of PMMA and the OH groups of epoxy. Kwei [15] confirmed the existence of hydrogen bonding between PMMA and epoxy Novolac prepolymers.

Moreover, the final properties of epoxy–PMMA cured blends also depend on the curing agent used. Hseih and Woo [10] observed, with DDS as hardener and 14 wt% PMMA, a phase inverted structure with epoxy microparticles in a PMMA-rich matrix. Gomez and Bucknall [11] focused on phase separation and noticed a complex morphology with large PMMA domains containing epoxy-rich sub-inclusions in an epoxy matrix, using 4,4′-diamino-3,3′-dimethyldicyclohexylmethane as the hardener. The case of an inverted structure, leading to an increase of the stress intensity factor $K_{\mathrm{IC}}$, has been observed by Galante et al. [16] using an anhydride-curing agent. Furthermore, Remiro et al. [17] studied the transparency of PMMA-modified epoxy using MDA as hardener. They noted that the phase separation process and consequently the size of the dispersed domains depend on the curing conditions. Similar conclusions have been obtained by Van Der Sanden and Jansen [18] who proposed particular curing conditions to obtain transparent thermoplastic-modified thermoset.

Core–Shell Rubbers (CSR) have been introduced in epoxy systems to increase their toughness [19]. Generally, the shell is based on PMMA. Surprisingly, nobody has introduced the effect of eventual solubility of PMMA with the matrix, whereas it should influence the quality of the dispersion and therefore the properties of the system.

The aim of this work is to investigate further the behavior of PMMA/epoxy blends using three different curing agents. Indeed, the hardener is expected to affect both the miscibility during polymerization reaction and the reaction rate. It will be shown that very different morphologies can be achieved according to the hardener used.

## 2. Experimental

### 2.1. Materials and sample preparation

Two types of epoxy monomer were used: a monoepoxy, phenyl glycidyl ether (PGE) from Sigma Aldrich and a diepoxy, DGEBA with an average number of hydroxyl groups per two epoxy groups of $\bar{n} = 0.15$ (LY556 from Ciba Geigy). The hardeners are three aromatic diamines: MCDEA (Lonza), DDS (Fluka) and MDA (Aldrich). The thermoplastic used was a syndiotactic PMMA from Elf Atochem. Average molar masses of PMMA were measured using size exclusion chromatography (SEC) with PMMA standards (American Polymer Standards Corp.). The resulting number average molar mass $\bar{M}_{\mathrm{n}}$ and polydispersity index values were 47,000 g mol$^{-1}$ and 1.4, respectively. The different characteristics and structures of materials are listed in Table 1.

The blends based on DGEBA and containing low thermoplastic amounts ($\leq 30$ wt%) were prepared using a glass reactor: DGEBA and PMMA are mixed in the reactor at 135°C. After about 3 h, the solution becomes homogeneous. The curing agent was then added to the transparent solution and mixing was stopped after approximately 5 min. Owing to high viscosity, blends with a PMMA content higher than 30 wt% were prepared by dissolving PMMA and DGEBA in methylene chloride. The solvent was removed at room temperature. To ensure complete removal, blends were left under vacuum for one night. As the two methods give

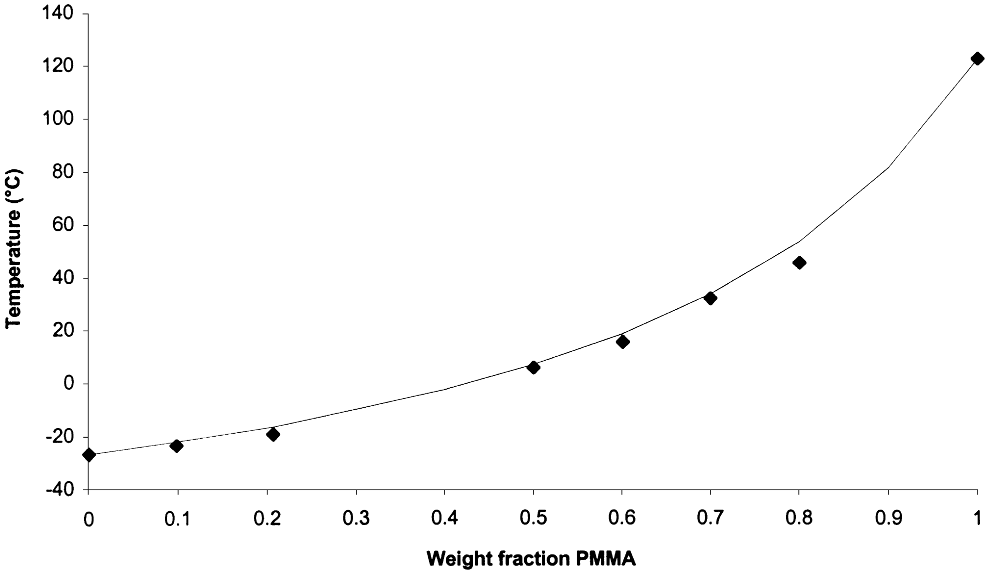


Fig. 1. Experimental (◆) and predicted (–) glass transition temperature versus mass fraction of PMMA for DGEBA $\bar{n} = 0.15$/PMMA blends. For prediction PMMA: $T_g = 122$°C, $\Delta Cp = 0.19\ J\ g^{-1}\ K^{-1}$ and DEGBA: $T_g = -27$°C, $\Delta Cp = 0.52\ J\ g^{-1}\ K^{-1}$.

homogeneous solution of unreactive blends, we can consider that they do not influence the final morphologies obtained. The hardener was always used at the stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1.

For blends with PGE, the monoepoxy was reacted first with MCDEA in bulk for 14 h at 135°C. The resulting product was then dissolved with 10 wt% PMMA in methylene chloride. The solvent in the PMMA/epoxy solution was first removed under vacuum at 20°C. The temperature was then increased slowly until all the solvent was completely removed.

### 2.2. Differential scanning calorimetry

The glass transition temperature $T_g$ and the change in heat capacity through the glass transition, ΔCp, were measured using a differential scanning calorimeter (Mettler TC10A). All measurements were made with a heating rate of 10°C min$^{-1}$.

Cured PMMA–epoxy blends were characterized using a TA 2920 modulated DSC instrument with a heating rate of 4°C min$^{-1}$. The experiments were performed in an only-heating condition with a modulation amplitude of 0.63°C and a 60 s period. In our case, the interest of modulated DSC is to provide better sensibility and resolution than conventional DSC [20].

### 2.3. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Magna 550 spectrometer in a transmission mode (KBr pellets, 32 scans, resolution 4 cm$^{-1}$). For all blends, the components were dissolved in appropriate proportions in methylene chloride and the solution was then cast onto potassium bromide pellets. The solvent was removed at room temperature for 48 h. Measurements were carried out with the potassium bromide pellets.

### 2.4. Size exclusion chromatography

Size exclusion chromatography (SEC) was used: (i) to investigate any change in the molar mass distribution of PMMA and (ii) to measure the epoxy conversion during curing of epoxy with amine. A Waters device equipped with a 6000A pump, a U6k-type injector and a double detection (UV at $\lambda = 254$ nm and a differential refractometer R401) was employed. The eluent was tetrahydrofuran at a flow rate of 1 ml min$^{-1}$ at 20°C.

The determination of epoxy group conversion supposes that both epoxy functions have equal reactivity. Then, considering that $X$ is the conversion of DGEBA molecules ($n = 0$) and $x$ the conversion of epoxy groups, $x$ is given by the equation

$$(1 - X) = (1 - x)^2 \tag{4}$$

The disappearance of the epoxy monomer, obtained with the SEC chromatogram, is

$$X = 1 - \left(\frac{H_t}{H_0}\right) \tag{5}$$

where $H_0$ and $H_t$ are the height of the DGEBA ($n = 0$) peak at $t = 0$ and at a time $t$ of reaction, respectively. Arranging Eqs. (4) and (5), the conversion of epoxy groups is given by:

$$x = 1 - \left(\frac{H_t}{H_0}\right)^{1/2} \tag{6}$$

The gel time is obtained from the appearance of an insoluble fraction in THF.

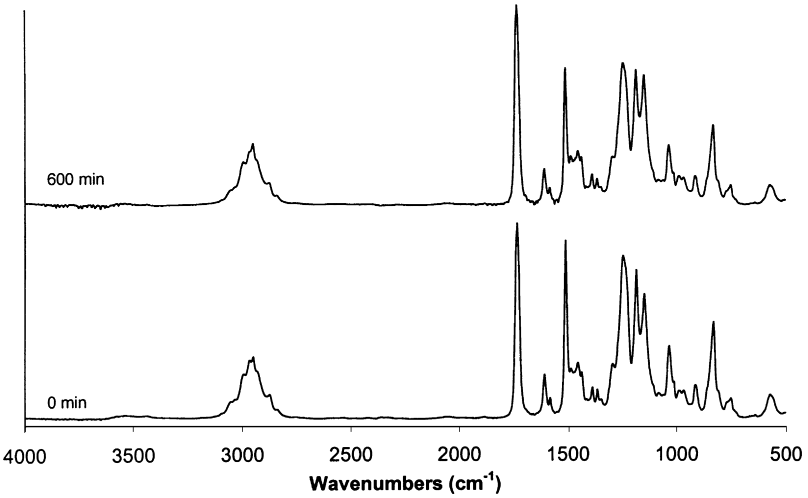


Fig. 2. FT-IR spectra of DGEBA $\bar{n} = 0.15$/30 wt% PMMA blend at 135°C.

### 2.5. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on cured blends with a Rheometrics Solid Analyser (RSA II) in order to obtain tensile dynamic mechanical spectra (storage modulus $E'$, loss modulus $E''$ and loss factor tan $\delta$) between 50 and 250°C at a frequency of 1 Hz. The samples used were parallelepipedic bars ($1 \times 2.5 \times 34\ \mathrm{mm}^3$).

### 2.6. Transmission electron microscopy

Ultrathin sections were obtained using an ultramicrotome at room temperature and were not stained. Transmission electron microscopy (TEM) was performed on a Phillips CM 120 microscope operating at 80 kV.

### 2.7. Cloud points measurements

The cloud point (CP) times have been determined using light transmission technique which detects particles with diameters higher than 100 nm and with a refraction index different from the matrix ($n = 1.49$ and 1.55 for neat PMMA and epoxy network, respectively). The CP time is determined at the onset time when the transmitted light intensity decreases.

## 3. Results and discussion

### 3.1. Initial miscibility

The glass transition temperature of unreactive DGEBA/PMMA blends with various PMMA concentrations have

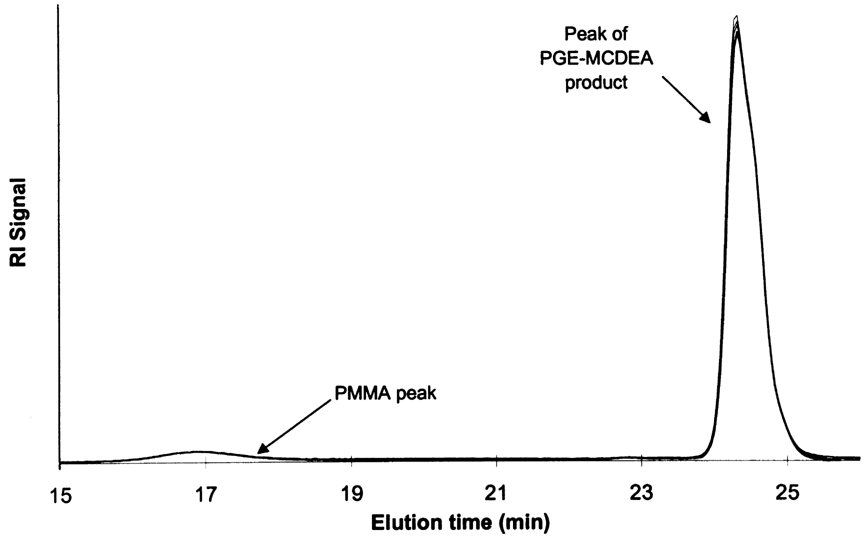


Fig. 3. Chromatogram of a PGE/MCDEA product reacted with 10 wt% PMMA at various reaction times at 135°C (from 0 to 10 h).

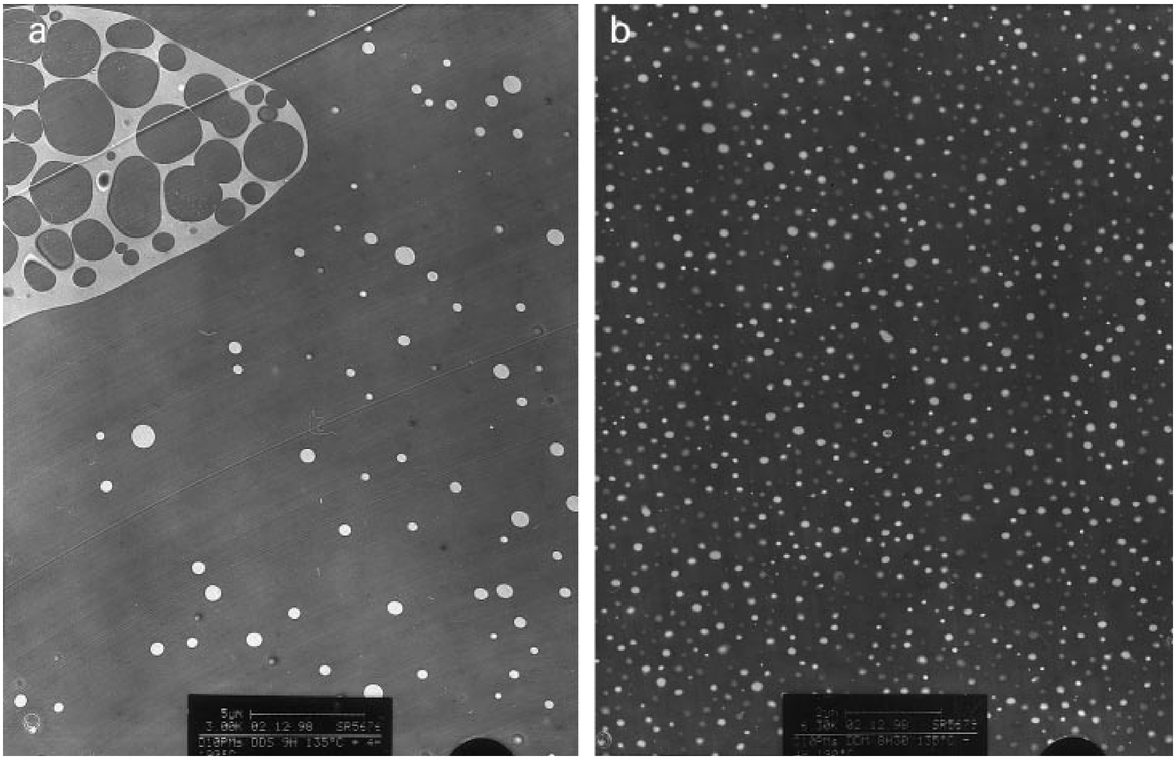


Fig. 4. Transmission electron micrographs obtained with 10 wt% PMMA blends using: (a) DDS; and (b) MDA hardener (curing schedule cf. text).

been measured by DSC. The visual transparency and the single $T_g$ on the whole composition range of the samples suggest complete miscibility of the polymer with the epoxy prepolymer. Fig. 1 shows the measured glass transition temperature versus weight fraction of PMMA.

In the case of miscible blends, the Couchman equation can be used to predict the $T_g$ of the system:

$$\ln T_g = \frac{M_1\,\Delta Cp_1 \ln T_{g1} + (1 - M_1)\Delta Cp_2 \ln T_{g2}}{M_1\,\Delta Cp_1 + (1 - M_1)\Delta Cp_2} \qquad (7)$$

with $T_g$, $T_{g1}$ and $T_{g2}$ the glass transition temperature of blend and components 1 and 2, $\Delta Cp_1$ and $\Delta Cp_2$ the heat capacity change at $T_g$ of components 1 and 2 and $M_1$ the mass ratio of component 1. The fit of the experimental points with the equation prediction in Fig. 1 supports the miscibility and homogeneity of the blend.

For blends containing 10 wt% PMMA, the addition of the diamine MCDEA, DDS or MDA at the stoichiometric ratio $a/e = 1$ does not induce any phase separation at zero conversion.

### *3.2. Possibility of specific interaction and trans-reaction during cure.*

The DSC results are not sufficient to detect any interaction between DGEBA and PMMA. Conversely, IR spectroscopy is a powerful technique of studying such interactions [12,13]. Three blends were characterized by FT-IR at 135°C: DGEBA/30 wt% PMMA, DGEBA/MCDEA/10 wt% PMMA and the product of reaction of PGE with MCDEA/10 wt% PMMA.

Fig. 2 displays the FT-IR spectra at 135°C of the binary DGEBA/30 wt% PMMA blend at different times. Increasing the heating time does not induce any shift or modification of the O–$CH_3$ (2850–2950 $cm^{-1}$) and the C=O (1725 $cm^{-1}$) peaks of PMMA. The spectra of the other blends are not presented here but the same results were obtained. Assuming the hydrogen bonding interaction between the carbonyl groups of PMMA and the hydroxyl groups of epoxy or epoxy–amine, a shift or broadening on the lower frequency side of the C=O peak would be expected. In the same way, a trans-esterification reaction of PMMA with epoxy prepolymer would decrease the height of the O–$CH_3$ peak of PMMA. These results indicate that PMMA does not undergo either specific interaction or trans-esterification with DGEBA at 135°C.

Another way to study a possible trans-esterification reaction between the hydroxyl groups of DGEBA or DGEBA/diamine copolymers and PMMA is to investigate the molar mass of the components of the system after heating. Two methods have been used.

1. Blends containing DGEBA, MCDEA and 10 or 30 wt% PMMA were cured at 135°C. SEC analysis were carried out on these blends at different reaction times. The chromatograms do not display any evolution of the PMMA peak (RI and UV detection). If the grafting of epoxy or epoxy–amine molecules on PMMA took place,

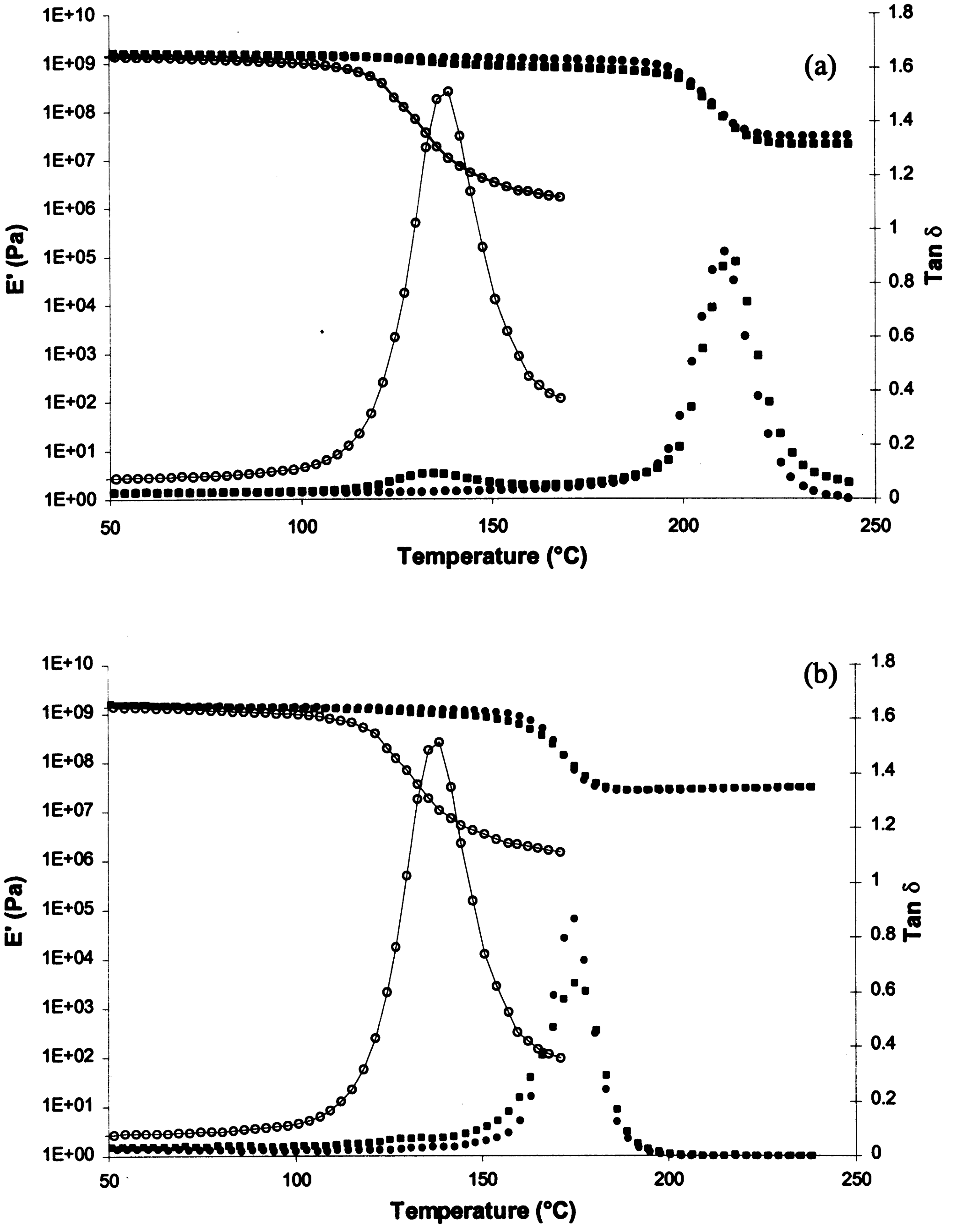


Fig. 5. Comparison between the dynamical mechanical spectra obtained with 10 wt% PMMA blends using: (a) DDS; and (b) MDA hardener, PMMA and the neat epoxy network. (a) (○) PMMA; (■)10 wt% PMMA/DGEBA/DDS 9 h–135°C + 4 h–190°C; (●) DGEBA/DDS 7 h–160°C + 4 h–190°C; and (b): (○) PMMA; (■) 10 wt% PMMA/DGEBA/MDA 19 h–135°C + 4 h–190°C; (●) DGEBA/MDA 6 h–190°C.

the molar mass of PMMA would be expected to increase. Furthermore, the grafting of aromatic cycles on the thermoplastic should enhance the UV response of the polymer, as the UV detection at 254 nm is very sensitive to the presence of aromatic groups. This phenomenon cannot be detected on these samples.

2. An alternative way to detect a trans-esterification reaction is to use a small molecule obtained by the reaction of a monoepoxy (PGE) with a diamine. The PMMA was then added and the blend was heated at 135° for 10 h. Fig. 3 displays partial SEC chromatograms showing the PMMA and PGE/MCDEA peaks at different times. No modification of the PMMA peak can be seen and the height of the PGE/MCDEA peak does not change at all, confirming that no epoxy–amine molecule has been grafted on PMMA and that no trans-esterification between PMMA and the secondary hydroxyl group of the epoxy-based molecule occurs at 135°C.

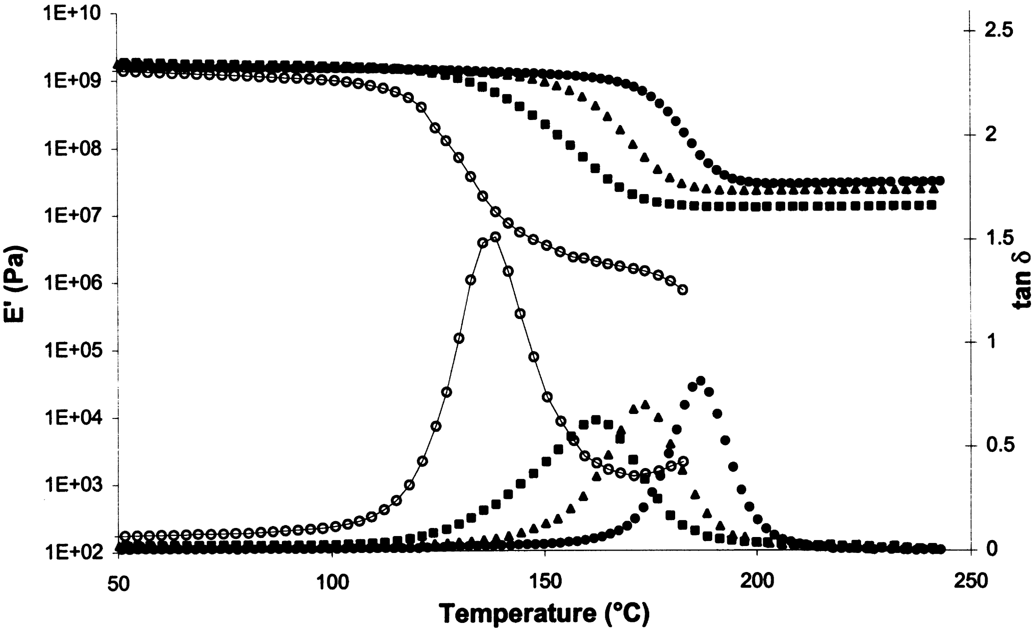


Fig. 6. Comparison between the dynamical mechanical spectra obtained with 10 and 30 wt% PMMA blends, PMMA and the neat epoxy network. (●) DGEBA/MCDEA 14 h–135°C + 4 h–190°C; (▲) 10 wt% PMMA/DGEBA/MCDEA 14 h–135°C + 4 h–190°C; (■) 30 wt% PMMA/DGEBA/MCDEA 19 h–135°C + 4 h–190°C; and (○) PMMA.

On the basis of both FT-IR and SEC results, we can conclude that no hydrogen bonding exists between PMMA and DGEBA and that no trans-esterification reaction occurs.

### 3.3. Morphologies of cured PMMA–epoxy network blends

TEM was carried out on samples containing 10 wt% PMMA and cured with the three diamines (Fig. 4a and b) at 135°C until gelation and vitrification and post-cured for 4 h at 190°C. The aim was to detect any phase separation between PMMA and the epoxy network, since samples appear fully opaque using DDS or MDA as hardeners but slightly cloudy with MCDEA. In the case of DDS-based blends (Fig. 4a), a complex structure can be seen with

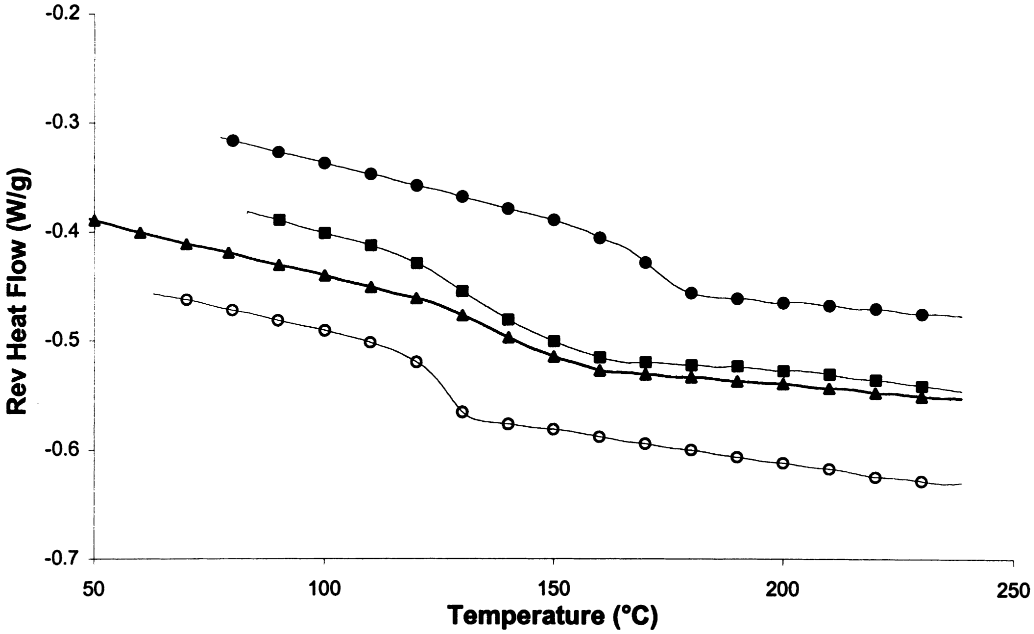


Fig. 7. Glass transition of the cured and post-cured DGEBA/MCDEA/30 wt% PMMA blends compared to those obtained for PMMA and the neat epoxy network. (○) PMMA; (▲) 30 wt% PMMA/DGEBA/MCDEA 19 h–135°C; (■) 30 wt% PMMA/DGEBA/MCDEA 19 h–135°C + 4 h–190°C; and (●) DGEBA/MCDEA 14 h–135°C + 4 h–190°C.

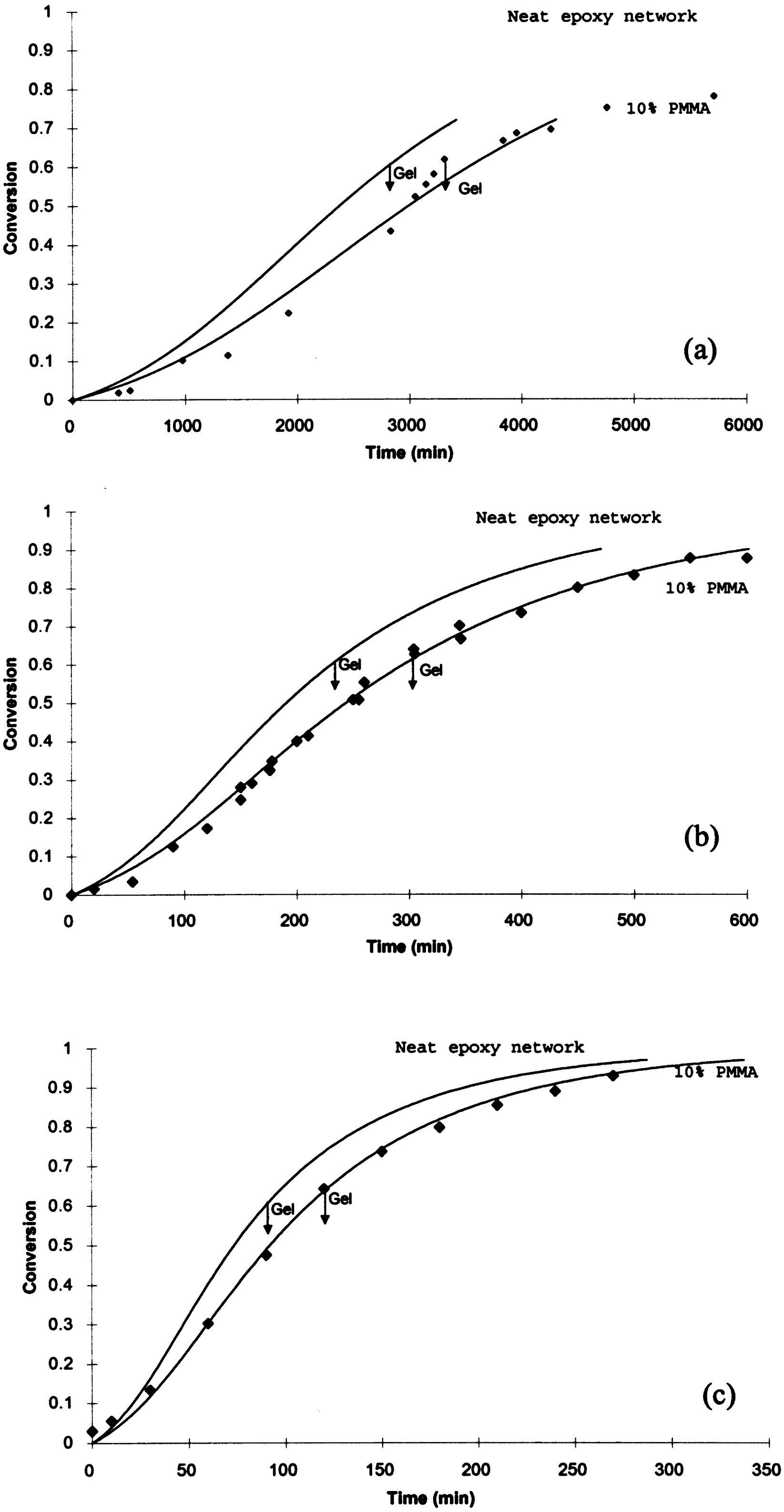


Fig. 8. Conversion of the epoxy–amine reaction of DGEBA/MCDEA/10 wt% PMMA blend measured by SEC at: (a) 80°C; (b) 135°; and (c) 160°C. Experimental points (◆) and model (–) taking into account the dilution effect of epoxy functions. Arrows (↓) indicate gel point observed by the first appearance of an insoluble fraction in THF.

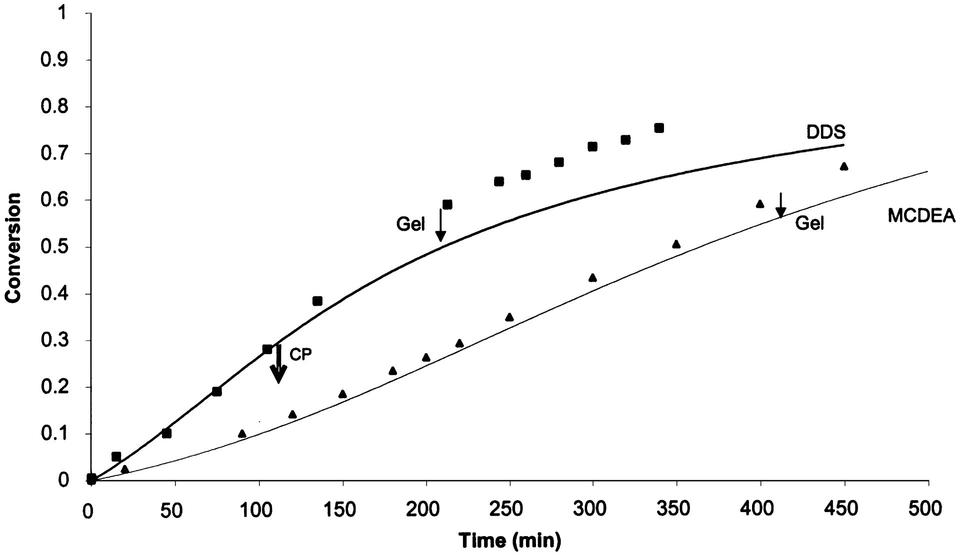


Fig. 9. Conversion of the epoxy–amine reaction measured by SEC and for 30 wt% PMMA/DGEBA/amine blends using (■) DDS or (▲) MCDEA as hardeners at 135°C; (–) model taking into account the dilution effect of epoxy functions. Arrows indicate the gel point (↓) observed by the method of insoluble and the cloud point (⇓) determined by light transmission.

small PMMA nodules in an epoxy matrix and large PMMA domains containing epoxy sub-inclusions. This morphology is typical of a blend composition close to the critical composition.

With regards to blends with MDA (Fig. 4b), the micrograph displays PMMA nodules dispersed in a thermoset matrix. For blends with MCDEA, no phase contrast can be seen and a homogeneous structure is suggested.

DMA and DSC were then carried out on the fully cured samples to further investigate the various morphologies observed by microscopy. The results of DMA carried out on cured samples, based on DDS and MDA hardeners, are given in Fig. 5a and b. The two-phase structure suggested by the opacity and the TEM results is confirmed by the two distinct relaxations observed on the tan $\delta$ curve. The low temperature relaxation corresponds to the relaxation of a PMMA-rich phase whereas the high temperature one corresponds to the relaxation of the epoxy-rich phase.

Fig. 6 presents the dynamical spectra of post-cured blends containing 10 and 30 wt% PMMA with MCDEA as the curing agent. The single relaxation located between the main relaxations of pure PMMA and the neat network, supports that the structure is homogeneous. Moreover, the relaxation peak is broad compared with those of pure components, indicating a large dispersion of relaxation times.

DSC scan for blend containing 30 wt% PMMA is given in Fig. 7 and is compared to those obtained for PMMA and the neat epoxy network. It clearly appears that adding PMMA to the epoxy network based on DGEBA/MCDEA, leads to a large single glass transition temperature comprised between those of pure PMMA and unmodified DGEBA/MCDEA network. However, the onset of the transition for blends seems to be at the same temperature as that of the syndiotactic PMMA. Thus, these results are consistent with a single-phase structure of the cured blend with perhaps local segregations at very short scales.

### 3.4. Kinetic study of PMMA-modified epoxies

The kinetic studies were carried out on two systems, one that does not present any phase separation on the final material using MCDEA as the hardener, and another presenting phase separation during curing, and based on DDS.

The chemical constant rates have been previously determined [14] for DGEBA $\bar{n} = 0.03$/MCDEA system, for reaction (1) (autocatalytic and non-catalytic mechanism) and for reaction (3):

$$K_{c1} = k_1 e_0^2 = 5.24 \times 10^5 \exp\left(-\frac{6975}{T}\right) \text{min}^{-1} \tag{8}$$

$$K'_{c1} = k'_1 e_0 = 2.15 \times 10^2 \exp\left(-\frac{6368}{T}\right) \text{min}^{-1} \tag{9}$$

$$K_{c3} = k_3 e_0^2 = 2.61 \times 10^2 \exp\left(-\frac{4383}{T}\right) \text{min}^{-1} \tag{10}$$

with $k_i$ = rate constant of equation $i$ and $e_0$ = initial concentration of epoxy function.

For DGEBA $\bar{n} = 0.03$/DDS, etherification reactions can be neglected ($K_{c3} = 0$) and the chemical constant rates for reaction (1) are:

$$K_{c1} = 3.96 \times 10^6 \exp\left(-\frac{7583}{T}\right) \text{min}^{-1} \tag{11}$$

$$K'_{c1} = 1.90 \times 10^5 \exp\left(-\frac{7583}{T}\right) \text{min}^{-1} \tag{12}$$

The ratio of the rate constants have been measured [14] and $r = k_2/k_1 = 0.65$ for DGEBA/MCDEA whereas $r = 0.45$ for DGEBA/DDS.

The use of DGEBA $\bar{n} = 0.15$ instead of DGEBA $\bar{n} = 0.03$ implies a slight dilution of epoxy functions and hence a small decrease of the reaction rate. The modified chemical rate constants should take this dilution effect into account:

$$K_{c1}(0.15) = \left(\frac{e_0(0.15)}{e_0(0.03)}\right)^2 K_{c1}(0.03) \tag{13}$$

$$K'_{c1}(0.15) = \left(\frac{e_0(0.15)}{e_0(0.03)}\right) K'_{c_1}(0.03) \tag{14}$$

with $e_0(i) =$ initial concentration of epoxy group for DGEBA $\bar{n} = i$.

Furthermore, taking into account the dilution effect induced by the addition of thermoplastic, the previous constants should be now corrected by the ratio $e_{0M}/e_{0N}$ of initial concentration of epoxy functions in modified ($e_{0M}$) and neat ($e_{0N}$) systems. This ratio can be expressed by the mass fraction of thermoplastic ($\Phi_{TP}$), the density of the epoxy–amine system ($\rho_N$) and of the thermoplastic ($\rho_{TP}$) as follows:

$$\frac{e_{0M}}{e_{0N}} = \left(1 + \frac{\Phi_{TP}}{1 - \Phi_N}\frac{\rho_N}{\rho_{TP}}\right)^{-1} \tag{15}$$

Fig. 8a–c presents both experimental points and model of epoxy conversion for the DGEBA/MCDEA/10 wt% PMMA blend taking into account the dilution effect at three different curing temperatures (80, 135 and 160°C). Arrows indicate gel times. It is worth reminding that all the samples appear slightly turbid after curing but no CP can be detected before gelation. The agreement between experimental and theoretical values indicates that the addition of PMMA only induces the expected dilution effect of reactive groups on the reaction rate. Similar conclusions could be drawn for the DGEBA/DDS/10 wt% PMMA blend though the sample was fully opaque at the end of the cure.

Secondly, concerning blends with 30 wt% PMMA, two different behaviors are observed according to the hardener used (see Fig. 9). With MCDEA, the theoretical curve and the experimental points are superimposed. On the other hand, an acceleration of the reaction rate occurs with DDS just after the phase separation ($t_{CP}$), determined by light transmission.

The same acceleration phenomenon at the CP has been observed by Bonnet et al. [7] for blends based on polystyrene (PS) or polyetherimide (PEI) (content 30 wt%) in DGEBA/MCDEA systems. In fact, the developed kinetic model can only be applied before phase separation in homogeneous medium. After phase separation, a dispersed phase is formed and two phases co-exist with unknown epoxy–amine concentration in each phase. Moreover, the dilution ratios change rapidly and differently in the epoxy rich and thermoplastic rich phases during phase separation and with reaction times. The experimental conversion that is measured after phase separation is an overall measurement $\bar{x}$ of conversions of both phases.

Looking back to Fig. 9, the fit of the prediction for blends based on DDS is good up to the phase separation phenomenon but then an increase of the reaction rate is observed: the previously observed reaction-induced phase separation occurs for this system. With regard to the blend containing 10 wt% PMMA, the reaction rate acceleration is probably not significant enough to be observed on the conversion curve. On the contrary, blends using MCDEA as the hardener do not phase-separate before gelation. The slightly turbid appearance of fully cured samples may result from an expulsion phenomenon owing to the network crosslinking density increase.

## 4. Conclusions

PMMA/DGEBA blends present a total miscibility over the whole composition range between the thermoplastic and the epoxy prepolymer. The FT-IR and SEC results reveal that neither specific interaction nor reaction takes place between PMMA and the thermoset components during curing.

Moreover, depending on the epoxy hardener used, the PMMA-modified epoxy network presents two behaviors:

1. On one hand, using DDS or MDA, the usual polymerization-induced phase separation occurs before gelation, leading to an acceleration of the epoxy–amine reaction rate during curing. The final opaque cured samples present a two-phase structure characterized by TEM and DMA.
2. On the other hand, using MCDEA as the hardener, no phase separation is noticed before gelation. The addition of PMMA only leads to the expected dilution effect of epoxy functions on the epoxy–amine reaction rate. The final cured samples appear slightly turbid and are characterized by a single broad relaxation in DMA and no phase contrast in microscopy. In that case, the PMMA is probably expulsed from the epoxy network after gelation at very small scales and so we really have what some call a semi IPN [21].

This result involves that the uncrosslinked PMMA-shell of CSR particles should be non-miscible in reacted epoxy systems based on DDS and MDA and miscible in the case of MCDEA as the hardener. This fact certainly strongly influences the quality of particle dispersion. It can explain clustering and aggregation of primary particles as observed in DGEBA/DDS systems [19]. On the contrary, a more homogeneous dispersion is expected in DGEBA/MCDEA system but unfortunately, there is no study in literature to confirm this point.

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