EPOXY/POLY(BENZYL METHACRYLATE) BLENDS: MISCIBILITY, PHASE SEPARATION ON CURING AND MORPHOLOGY

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Diglycidyl ether of bisfenol-A (DGEBA)/polybenzyl methacrylate (PBzMA) blends cured with 4,4'-diaminodiphenylmethane (DDM) were studied. Miscibility, phase separation, cure kinetics and morphology were investigated through differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Non-reactive DGEBA/PBzMA blends are miscible over the whole composition range. The addition of PBzMA to the reactive (DGEBA+DDM) mixture slows down the curing rate, although the reaction mechanism remains autocatalytic. On curing, initially miscible (DGEBA+DDM)/PBzMA blends phase separate, arising two glass transition temperatures that correspond to a PBzMA-rich phase and to epoxy network. Cured epoxy/PBzMA blends present different morphologies as a function of the PBzMA content.

Introduction

Many studies have dealt with the modification of epoxies adding a rubber or a thermoplastic polymer in order to improve toughness [1–3]. Ductile, high glass transition temperature (T_g) thermoplastics have been reported as effective toughness modifiers of epoxies [4–9]. The initial mixture consists of a thermoplastic dissolved in the epoxy resin precursor (epoxy monomer+curing agent). On curing, the blends phase separate, giving rise to different morphologies as a function of the thermoplastic content. The mechanical properties of the cured system are related to morphology, which depends on the curing conditions and on the thermoplastic content [1–13].

Poly(vinyl acetate) (PVAc) which is a ductile thermoplastic with a moderate T_g~44°C has been also reported to improve toughness of epoxy resins [10]. In previous works [14–16] we have studied the curing of epoxy/PVAc blends. Moreover blends of epoxy with polymethyl methacrylate (PMMA) T_g~110°C have been the subject of several studies [11–13]. In the present work polybenzyl methacrylate (PBzMA), which has T_g value intermediate between those of PVAc and PMMA, has been selected as modifier of epoxy thermoset based on diglycidyl ether of bisfenol A (DGEBA). In the system epoxy/PBzMA good interactions between ether groups of epoxy and phenyl groups of PBzMA would take place, affecting the initial miscibility and phase separation on curing. The aim of this work is to examine the miscibility of non reactive DGEBA/PBzMA blends and the induced reaction phase separation when 4,4'-diaminodiphenylmethane (DDM) is used as curing agent. The effect of the thermoplastic on the cure reaction, and morphology of the generated materials is investigated using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

Experimental

Materials and blend preparation

The epoxy prepolymer, DGEBA, was supplied by Ciba under the commercial name of Araldit F. The number average relative molecular mass M_n=380 g mol^{-1}. The curing agent, DDM, was manufactured by Aldrich (97 mass%). PBzMA with M_w=7·10^4 g mol^{-1} was purchased from Polysciences. Acetone Panreac QP (0.3 mass% water content) was used as solvent.

DGEBA and DDM were used with a stoichiometric ratio amino-hydrogen to epoxy. Three solutions were prepared: DGEBA, PBzMA and DDM in acetone. Blends of DGEBA/PBzMA, and (DGEBA+DDM)/PBzMA were obtained by mixing appropriate amounts of these solutions. Non reactive DGEBA/PBzMA blends were cast into aluminium

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DSC pans and dried under vacuum at 85°C (5–6 h). Reactive (DGEBA+DDM)/PBzMA blends, having different amounts of PBzMA, were cast into aluminium pans and dried under vacuum, 20 h at 40°C, in order to prevent curing reaction. After drying, non reactive and reactive samples reached constant mass and their DSC scans did not show any evaporation endothermic peak, confirming that acetone had been removed. Reactive dried samples were cured at T_c=120°C under atmospheric pressure.

Methods

DSC measurements

A Mettler Toledo mod.822e differential scanning calorimeter was used to measure the glass transition temperatures and heats of reaction. All measurements were done at a heating rate of 20°C min^{-1}, under nitrogen atmosphere. The instrument was calibrated with indium and zinc. Samples of 10–20 mg were used.

To study the miscibility of the non reactive DGEBA/PBzMA blends they were scanned from –40 to 200°C determining glass transition temperatures. The T_g was taken at the midpoint of the heat capacity change.

In order to get the evolution of T_g and conversion (α) upon curing reactive samples (DGEBA+DDM)/PBzMA, they were cured in an oven at 120°C for various time intervals, so different degrees of cure were achieved. After that, the samples were rapidly cooled and scanned from –50 to 300°C. The residual heat of reaction (ΔH_r) was calculated as the area of the exothermal peak of the DSC scans. The degree of conversion was obtained as:

$$\alpha = \frac{\Delta H_t - \Delta H_r}{\Delta H_t} \qquad (1)$$

where (ΔH_t) is the total heat of reaction obtained from the area of the exothermal peak of uncured samples.

T_gs of phases in the samples were obtained also from the DSC scans. The glass transition of PBzMA (T_g~60°C) is much lower than the T_g of the epoxy network. Therefore, in this system it is feasible to follow the induced reaction phase separation through T_g monitoring.

ESEM measurements

Due to the non conducting nature of the specimens, the environmental scanning electron microscopy (ESEM) mode was used to study the morphology of the cured samples. A Phillips XL30 instrument was employed with a beam energy of 20 kV, verifying that this did not produce severe damage on the samples. The water vapour pressure was 0.6–0.7 Torr, that corresponds to a relative humidity of ~5%.

Results and discussion

Non reactive DGEBA/PBzMA blends

At room temperature DGEBA/PBzMA blends were transparent over the whole composition range, indicating complete miscibility. This conclusion was confirmed by DSC measurements: each blend showed a single T_g intermediate between the T_g values of the pure components. Figure 1 shows the variation of T_g with the blend composition expressed as the fraction mass of PBzMA. The T_g behaviour of ideal mixtures can be predicted by the Fox rule [17]:

$$\frac{1}{T_g} = \frac{(1-w_2)}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (2)$$

where w_2 represent the mass fraction of PBzMA in the blend, w_{PBzMA}, and T_{g1}, T_{g2}, and T_g refer to the T_g of DGEBA, PBzMA and the blend of composition w_2 respectively. Figure 1 also shows the Fox calculated curve for this blend, as can be seen, the predicted values are higher than experimental ones. A best fit can be obtained using Gordon-Taylor equation [18]:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (3)$$

with a value for the adjustable parameter k=0.33 indicating that the interactions between components are weak, although stronger than the interaction in DGEBA/PMMA for which it had been reported k=0.20 [13] and weaker than in DGEBA/PVAc which T_gs behaviour is well predicted by Fox rule [14].

Reactive (DGEBA+DDM)/PBzMA blends: conversion and T_gs

Reactive (DGEBA+DDM) blends containing different amounts of PBzMA have been studied by DSC. As PBzMA is used as epoxy modifier only samples
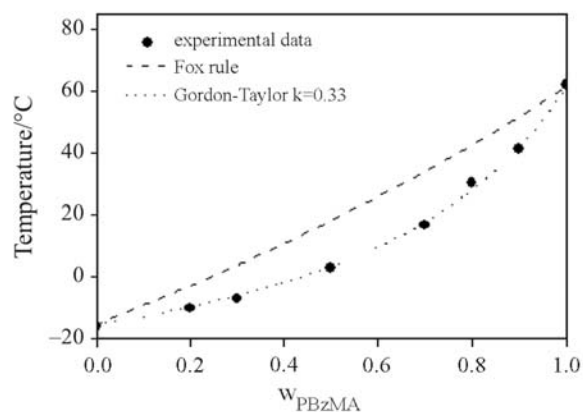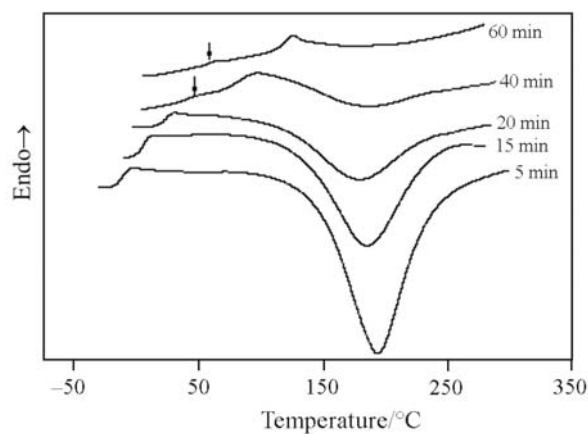

Fig. 1 T_g *vs.* mass fraction of PBzMA in non reactive blends DGEBA/PBzMA

having low content of PBzMA have been prepared. The selected compositions were w_{PBzMA}=0.05, 0.1 and 0.15, i.e. expressed as mass percentage: 5, 10 and 15 mass% of PBzMA. Hereafter the samples will be identified by mass% of PBzMA. These samples were cured at 120°C for different times (t_c), after that they were scanned in the DSC to determine the glass transitions and the residual heats of reaction. Figure 2 shows some of the scans obtained for blends (DGEBA+DDM)/15 mass% PBzMA. The steps in the heat flow are related to the T_gs of the phases present in the samples, these are followed by a broad exothermal peak that corresponds to the curing reaction heat. The conversions have been calculated using Eq. (1). Figure 3 shows the conversions *vs.* time plots for blends having 5, 10 and 15 mass% PBzMA, together with the data for neat epoxy [16]. For this cure temperature the conversion reaches values of α~0.94–0.98 after 2 h, no full curing is obtained because vitrification of the samples takes place around 60–70 min. When postcuring at T_c=150°C for 30 min full curing is reached in all the blends. As can be seen PBzMA

slows down the cure reaction, this could be related to the dilution effect of reactants. However it was not found a clear correlation between the PBzMA content and the delaying effect.

The general equation assumed for the isothermal curing reaction of epoxy-amine systems is [19]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (4)$$

where k_1 and k_2 are apparent rate constants and m, n are the reaction orders. k_1 represents the kinetic rate constant for the reaction catalysed by groups initially present and k_2 represents the kinetic rate constant associated with the autocatalysis by the –OH groups generated in the epoxy-amine reaction. On applying the kinetic model, only the data up to 60 min (α<0.92) were considered, because at that moment vitrification takes place and the reaction becomes diffusion controlled. Figure 4 shows the $d\alpha/dt$ *vs.* α plots, the curing reaction is autocatalytic, displaying maximum rates at conversions 0.25–0.29. The presence of PBzMA clearly decreases the reaction rate, but there is not a clear correlation with the PBzMA content, maybe due to the influence of phase separation that takes place during curing as it will be further discussed. The values of the model parameters determined by iterative procedure are listed on Table 1. The k_1 values are very low, indicating initial reaction rate close to zero. The k_2 values for the blends are lower than for neat epoxy, but the differences among blends are very slight. The reaction orders m and n are

Fig. 2 DSC scans for (DGEBA+DDM)/15 mass% PBzMA blends after being cured at 120°C different times. The arrows indicate the T_g of the PBzMA enriched phase
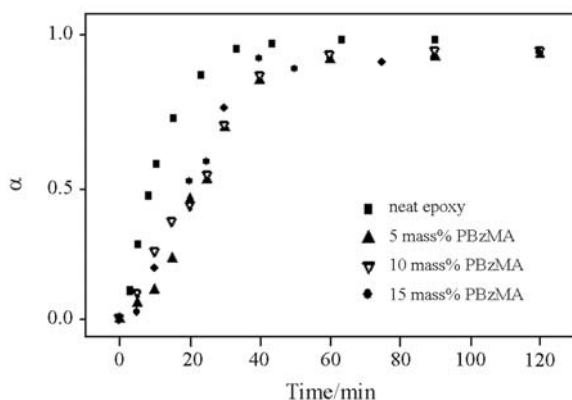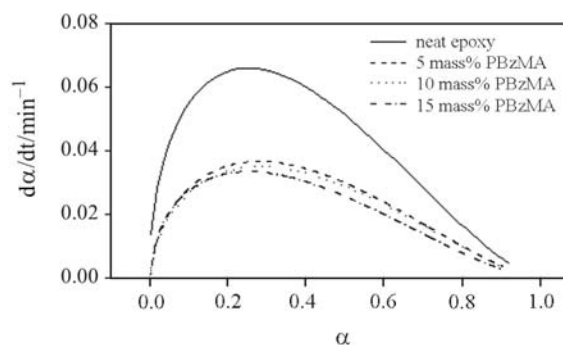

Fig. 3 Conversion *vs.* time for (DGEBA+DDM)/PBzMA with different PBzMA content (T_c=120°C)

Fig. 4 $d\alpha/dt$ *vs.* α plot for (DGEBA+DDM)/PBzMA with different PBzMA content (T_c=120°C)
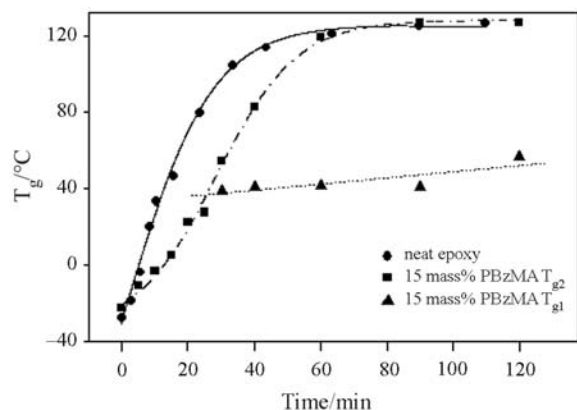
Table 1 Kinetic parameters for epoxy (DGEBA+DDM)/ PBzMA blends cured at 120°C

PBzMA/mass%	$k_1\cdot10^5/$ s^{-1}	$k_2\cdot10^3/$ s^{-1}	m	n
0	1.0	3.4	0.53	1.50
5	0.2	2.1	0.58	1.48
10	0.2	2.0	0.59	1.47
15	0.1	1.8	0.53	1.55

approximately 0.55 and 1.50 respectively and do not seem to vary with composition and the total reaction order $m+n$ was close to 2. These values are in accordance with the previously reported in the literature for epoxy cured with aromatic diamine [15, 16, 20, 21].

From the DSC scans of the reactive blends the T_g of the phases present in the samples were determined (Fig. 2). T_g *vs.* cure time for 15 mass% PBzMA blend and neat epoxy are plotted in Fig. 5. The neat epoxy presents a single T_g over all the curing process that increases with curing time. The blend presents a single T_g at the first stages of reaction ($t_c \leq 30$ min), that indicates the existence of a unique miscible phase, this T_g increases with time as a consequence of the increase of molecular mass of the epoxy as curing proceeds. For samples cured longer times ($t_c > 30$ min) two glass transitions are detected. The detection of these T_gs is coincident with the appearance of opacity in the samples, confirming that phase separation has taken place. The highest T_g (T_{g2}) increases with reaction time and after two hours reaches a final value ($T_g \sim 125°C$) very close to the T_g of the neat epoxy cured at the same temperature ($T_c=120°C$), so this phase should be composed basically by cured epoxy (DGEBA+DDM). The lowest T_g (T_{g1}) is close to PBzMA T_g (61°C), therefore it could be assigned to a phase essentially composed by PBzMA. T_{g2} takes values ~20°C lower than the PBzMA T_g when phase separation is first detected (30–40 min), therefore it could be inferred that some low molecular mass epoxy molecules have been drag along PBzMA acting as plastizisers, but at the end of curing a value $T_{g2} \sim 57°C$ is reached. The other blends (5 and 10 mass% PBzMA) present a similar T_g-time profile.

When the curing reaction is kinetically controlled there must be a one to one relationship between T_g and α. The relationship prop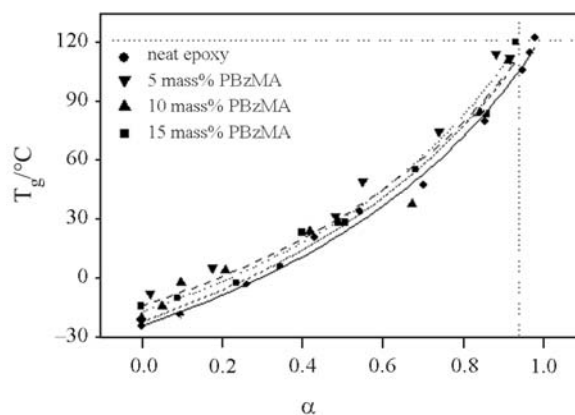osed by Pascault and Williams [22], considers the thermoset-ting system as a mixture of fully cured network and monomer:

$$\frac{T_g - T_g^0}{T_g^\infty - T_g^0} = \frac{\lambda\alpha}{1-(1-\lambda)\alpha} \tag{5}$$

where T_g^0 is the glass transition temperature of the unreacted mixture ($\alpha=0$), T_g^∞ the glass transition temperature of the fully reacted thermoset ($\alpha=1$) and λ is an adjustable parameter. This equation has been successfully used to fit the T_g–α behaviour of thermosets [22, 23]. In order to apply Eq. (5), the glass transition temperature of the fully reacted epoxy was determined on neat epoxy samples cured at 120°C for 2 h and postcured at 180°C for 1 h, the value obtained was $T_g^\infty=145°C$. T_g^0 is the initial T_g for each blend, which increases with PBzMA content. In Fig. 6 the experimental results of T_{g2} *vs.* conversion are plotted for all the blends, only the data corresponding to non vitrified samples ($T_g<T_c=120°C$) are considered, because from that point, the reaction becomes diffusion controlled. The lines on Fig. 6 represent the fits of Eq. (5) for each blend composition. The λ values obtained are in the range 0.40–0.55 which agree with the previously reported data for several amine epoxy systems [3, 15, 22, 23]. For samples with $\alpha<0.5$ the reactive system is a miscible blend of the growing epoxy molecules and PBzMA molecules, from $\alpha>0.5$ phase separation of PBzMA has already occurred and the T_{g2} reflects the growing epoxy. Therefore the major differences between the T_g–α correlations of the blends and neat epoxy occur when $\alpha<0.5$. As the PBzMA T_g is higher (61°C) than T_g of DGEBA (–27°C), at the first stages of curing ($t<30$ min, $\alpha<0.5$) the T_gs of the blends are above the ones of the neat epoxy.

Fig. 5 T_g *vs.* curing time for neat epoxy and (DGEBA+DDM)/15 mass% PBzMA blends cured at 120°C

Fig. 6 T_g of epoxy rich phase *vs.* conversion for (DGEBA+DDM)/PBzMA with different PBzMA content (T_c=120°C), experimental points and Pascault-Williams fits: (—) – neat epoxy, (· · ·) – 5 mass% PBzMA, (× – × – × –) – 10 mass% PBzMA and (– – –) – 15 mass% PBzMA
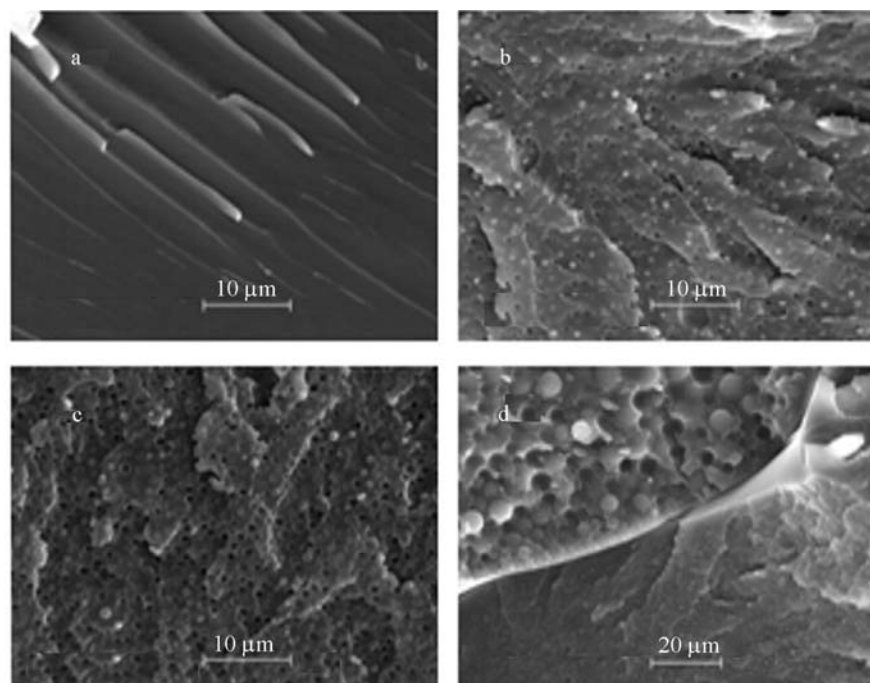
Fig. 7 ESEM micrographs for cured (DGEBA+DDM)/PBzMA samples (T_c=120°C, 2 h): a – neat epoxy, b – 5 mass% PBzMA,
   c – 10 mass% PBzMA, d – 15 mass% PBzMA

Morphological analysis of cured blends

Environmental scanning electron microscopy (ESEM) has been used to study the change in morphology of the cured blends with PBzMA content. Figure 7 shows the micrographs obtained for cured samples (2 h, 120°C). Neat epoxy shows homogeneous morphology with no visible phase domains. Blends with 5 and 10 mass% PBzMA are formed by an epoxy matrix, being the PBzMA phase dispersed as small spheres. However in samples containing 15 mass% of PBzMA phase inversion appears and it results in a combined morphology formed by regions in which PBzMA spherical domains are dispersed in an epoxy matrix (similar to the 5 and 10 mass% PBzMA morphology) together with regions with inverted morphology (epoxy spheres in a thermoplastic matrix). These morphologies are similar to the ones observed in epoxy/PVAc blends [15, 16]. The composition at which inversion in morphology takes place should be close to the critical point φ^c_{PBzMA}. The critical point has been calculated according to Pascault-Williams [1] using the relation:

$$(\varphi^c_{TP})^{-1} = 1 + \left[\frac{V_{TP}}{V_{TS}}\right]^{1/2} \frac{x_w(\text{TP})}{(x_z(\text{TP}))^{1/2}} \qquad (6)$$

where ϕ^c_{TP} is the volume fraction of the thermoplastic (PBzMA) at the critical point, V_{TP} is the molar volume of the repeating unit of the thermoplastic and V_{TS} is the molar volume of the thermoset precursor taken as a single pseudomonomer (2/3 mol DGEBA and 1/3 mol DDM), and $x_w(\text{TP})$ and $x_z(\text{TP})$ are the degrees of polymerization of the thermoplastic. The molar volumes where obtained from the densities and the polymerization degrees from GPC. The value calculated: $\varphi^c_{PBzMA} \sim 0.08$ is slightly lower than the experimental observation, i.e. the inversion in morphology takes place around $w_{PBzMa} \sim 0.15$, it should be noted that in this blend mass fraction and volume fraction are almost coincident because the densities of the components are very similar. Equation (6) was deduced from the theory of Flory-Huggings and it does not takes into account interactions between components, therefore the difference between experimental and calculated φ^c_{PBzMA} could mean that not only combinatorial effects lead the phase separation process and that interactions between PBzMA and epoxy although weak influence the induced reaction phase separation.

Conclusions

Non reactive DGEBA+PBzMA blends are miscible and the T_g-compositon can be fitted to Gorgon-Taylor equation with parameter k=0.33 revealing weak interactions between components.

The curing process of epoxy (DGEBA+DDM)/ PBzMA blends at 120°C was studied. The curing reaction is autocatalytic with maximum rates at conversions close to 0.25–0.29. The presence of PBzMA slows down the kinetics, but the autocatalytic reaction mechanism remains unaltered, being the total reaction order close to 2. The evolution of T_gs on curing re-

veals that the blends are initially miscible and phase separate on curing. The detection of two T_gs, is consistent with a biphasic morphology formed by a phase enriched in PBzMA and an epoxy rich phase. The T_g corresponding to the epoxy phase varies with conversion according to the Pascault-Williams relationship.

ESEM was used to study the morphology of cured samples. Blends with 5 and 10 mass% PBzMA are constituted by an epoxy matrix with PBzMA phase dispersed as small spheres. The inversion in morphology occurs when the PBzMA content reaches 15 mass% and it results in a combined morphology.

Acknowledgements

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