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ORIGINAL CONTRIBUTION

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Cure process and reaction-induced phase separation in a diepoxy–diamine/PMMA blend. Monitoring by steady-state fluorescence and FT-IR (near and medium range)

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Abstract Poly(methyl methacrylate), PMMA, was chosen as an additive for an epoxy system based on the cured product of (a) diglycidyl ether of bisphenol A labeled with 5-dimethylaminonaphthalene-1-(2-aminoethyl) sulfonamide and (b) 1,5-diamino-2-methylpentane. Fourier transformed infrared spectroscopy (near, FT-NIR, and medium, FT-MIR, ranges) and steady-state fluorescence spectroscopy were used to monitor the epoxy cure reaction and the induced phase separation. The PMMA seems to exert a change in the mechanism of the epoxy cure reaction by means of a slight enhancement of the secondary amino group reactivity. It has been demonstrated that following the fluorescence response of the dansyl chromophore chemically bonded to the epoxy component is a way to monitor the cure process in a general sense, not only accounting for the chemical changes but also being additionally possible to detect the reaction-induced phase separation at a molecular scale. The fluorescence results, in terms of the first moment of the emission band, point out that the dilution effect is affecting the physicochemical changes of the modified epoxy system quite more exclusively than the chemical changes. Finally, a semiempirical model to explain the behavior of the dansyl fluorescence during the curing of a PMMA/diepoxy–diamine blend showing a reaction-induced phase separation has been proposed. The proposed model allows estimating the composition of the phases after nearly complete cure.

Keywords Fluorescence · Blends · Epoxy curing

Introduction

The importance of polymer blends is associated to the variety of properties that can be obtained. Among others, these properties are a function of several factors: the constituents of the blend, the composition, and the mixing conditions. In fact, those properties are a consequence of the macromolecules' nature in the mixture and their mutual interactions, which are responsible for the morphologies that can be obtained. In general, most of the researches related with the study of polymer blends focused their interests on designing and controlling these morphologies. To have the experimental data necessary to establish a thermodynamic model, it is critical to look for an experimental technique or method capable of giving information about the phase separation, if it is the case, and even monitor it at a molecular scale.

In the last two decades, modified epoxy systems have been the objective of many studies (toughened epoxies for adhesive coatings and composites) [1]. The addition of high or relatively high glass transition temperature (T_g) thermoplastics generally increases their toughness, improves their poor resistance to crack propagation, keeping a high T_g, and reduces thermal stresses [1–4]. Morphology is a significant factor influencing the properties of modified epoxy mixtures [1, 5–9]. From an experimental point of view, when reaction-induced phase separation occurs [5], it would be essential to be able to know the composition of each phase in every moment since it might give the information required to establish the mechanism from which the final morphology is obtained and to explain certain properties that might be due more to the domain composition or to the interfacial adhesion between domains than to the morphology itself. To improve significantly the toughness, it is thought that there must be a strong interaction between domains at the interphase [3, 4, 10], maintaining a certain morphology. Probably, among the nature of the components, the incorporation of reactive end groups in the components of the polymer blend [10], the composition of the different phases, and the use of block copolymers [11] may be the important aspects to improve the interfacial adhesion. However, in those cases, it seems not possible to vary just the adhesion and keep exactly the same morphology [5].

There is no general method to obtain a particular domain size distribution and composition of dispersed phase particles to yield the maximum enhancement of the properties required for a specific application of the thermosetting polymer. A relatively easy method to vary morphologies is to change the cure conditions, for instance, changing the cure temperature. However, the effect of cure temperature in the final morphologies and final properties of the blends is very difficult to analyze. An increase of the cure temperature produces three different effects: an increase of the reaction rate, a decrease of the viscosity, and an increase (UCST) or decrease (LCST) of the initial miscibility. To clarify all these aspects, it is necessary to find a new method that allows monitoring simultaneously the cure process of the modified epoxy system, the phase separation or separations, if it is the case, and the composition of the different domains generated.

The beginning of the phase separation process can be determined by different techniques and methods such as light transmission (LT), light scattering (LS), or small-angle x-ray scattering (SAXS). Depending on the technique used, the observation scales can be different. Perhaps, looking for a reference starting point for the phase separation, it would be better to use a technique sensible to this phenomenon at a molecular scale. FT-IR (mid- and near range) [12–15], differential scanning calorimetry (DSC) [16, 17], and dielectric and mechanical measurements [14, 18, 19] are probably the most used techniques to study the advancement of cure reaction and the phase separation process in modified thermosetting polymers. Only the dielectric sensor has been described as to be used both in the laboratory as well as in situ in the fabrication tool in a production environment [18]. However, none of the mentioned techniques allows monitoring "in situ," "online," if it was necessary, nondestructively, and at a molecular scale not only the cure process and phase separation but also the compositional variation of each phase in an easy way.

There are many studies which have shown the use of fluorescence (intrinsic and extrinsic by means of fluorescence probes and labels) as a very good method for monitoring polymerization processes at a molecular scale, in situ, and in a nondestructive way [15, 17, 20–34]. Among the different photophysical characteristics of the chromophores used for monitoring cure processes, or polymerizations in general, those associated to changes in shape of the fluorescence spectra such as an intensity ratio [23, 26, 27, 29, 30, 32] or the first moment of the fluorescence emission band [15, 29–31] are preferred since they are generally unaffected by experimental conditions such as intensity fluctuations of the excitation light, changes in the excitation area, changes in the sample thickness, geometry of the device, etc. However, there are many works that use just the fluorescence intensity to monitor the polymerization processes. Generally, apart from quenching phenomenon, the variations in the fluorescence intensity can be due to (1) a microviscosity enhancement of the medium, which leads to a decrease in the nonradiative decay rate and, consequently, a substantial increase in the fluorescence quantum yield [20], or (2) chemical changes of the fluorophore [24]. However, these methods do not eliminate the effect of intensity variations arising from the external factors mentioned.

There are certain fluorescent groups such as dansyl derivatives (DNS) [15, 17, 26, 29–31, 34, 35] that show appreciable shift in their fluorescence emission band depending on the polarity and/or rigidity of their surroundings (solvatochromism). Therefore, their spectral shifts seem to be good photophysical parameters to monitor whatever the changes appearing at a molecular scale in polymeric systems, for instance, the physicochemical changes along a cure reaction and even a phase separation if one of the components that phase separates is specifically labeled with the fluorescent group.

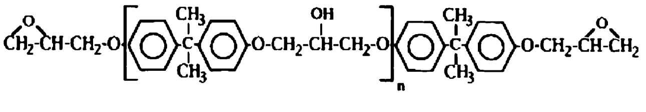
In this work, poly(methyl methacrylate), PMMA, was chosen as a thermoplastic additive for an epoxy system based on the cured product from diglycidyl ether of bisphenol A, DGEBA, and an aliphatic diamine. This system gathers several characteristics that make it a good candidate to be a model system to the further understanding of general behavior of thermoplastic modified epoxy systems. There is good miscibility between PMMA and the thermosetting precursors at room temperature and phase separation during subsequent cure at relatively low temperature. The aim of this work is to use FT-IR and steady-state fluorescence spectroscopy to monitor epoxy cure reaction and phase separation. Particularly, this study represents the first one in which the fluorescence response from chromophores chemically bonded to specific sites is used to monitor simultaneously at a molecular scale, in situ, and nondestructively a cure process and a subsequent reaction-induced phase separation, being able to estimate additionally the evolution of each phase composition. These processes will be studied at different temperatures to carry out the corresponding kinetic analysis associated to the cure reaction (influence of the presence of PMMA modifier) and to the phase separation. Finally, the data obtained from FT-IR, (1) in the near range to monitor the cure reaction and (2) in the medium range to monitor phase separation, will be used to complement this new information arising from the fluorescence study.

Experimental section

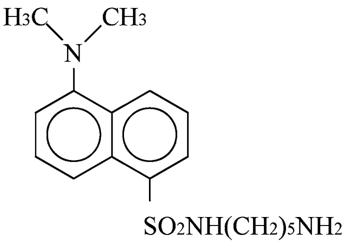
Materials and sample preparation

Poly(bisphenol A-co-epichlorohydrin) glycidyl end-capped (DGEBA, Aldrich Co.), **I**, $\langle M_n \rangle$=348 g/mol (n=0.03), was dansyl-labeled and treated with 5-dimethylaminonaphthalene-1-(2-aminopenthyl) sulfonamide (DNS-CAD, Aldrich Co.), **II**, following the procedure already described [29]. With this procedure, it was attached to one naphthalene sulfonamide group per 2.5×10^5 epoxy groups.

A model thermoplastic modified epoxy system, epoxy–PMMA, was prepared by mixing PMMA (Polysciences, Inc.), with a molecular weight average number of $\langle M_n \rangle$= 75,000 and a polydispersity of Γ=2.8, with the dansyl-labeled DGEBA and 1,5-diamino-2-methylpentane (DAMP, Fluka Chemika), **III**, in a stoichiometric ratio. The composition studied for the modified epoxy system was 2% w/w of PMMA. Furthermore, as a control sample, the labeled DGEBA/DAMP without PMMA was prepared in the same conditions for comparison (neat epoxy system).



I



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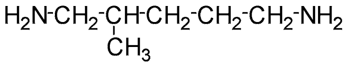

$H_2N\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

III

To prepare the initial reactive mixture for the modified epoxy, the PMMA is firstly blended at 120°C with the DGEBA by stirring with a magnetic bar for at least 10 h, ensuring that the solution is clearly transparent. After that, the DAMP is added to the homogeneous mixture PMMA/DNS-EDA-labeled DGEBA at room temperature, vigorously stirred with spatula for less than 2 min, and located in the oven in which the cure process is to be carried out. All the reactive mixtures were cured at different temperatures (50, 60, 70, and 80°C), stopping the reaction when the conversion reached almost a constant value.

Instrumentation

The curing process was followed using two different techniques: (1) Fourier transformed infrared spectroscopy in both the near range (FT-NIR) and the medium range (FT-MIR) and (2) steady-state fluorescence spectroscopy.

The FT-NIR and FT-MIR spectra were recorded with an FT-IR Spectrum GX (Perkin-Elmer) using a homemade program to collect spectra as a function of time. They were recorded at a resolution of 4 cm^{-1} and five scans. The curing reaction was monitored at 50, 60, 70, and 80°C using a temperature controller (SPECAC). In the case of FT-NIR experiments, the reactive mixtures were placed between two microscope–glass slide plates with an optical path of approximately 0.6 mm of thickness, determined by the thickness of a Teflon spacer, while in the case of FT-MIR experiments, the reactive mixtures were placed between two KBr pellets, ensuring a small optical path, avoiding therefore problems of absorption bands saturation and being in the Beer's interval. To obtain the areas of the selected bands for the analysis of the cure process, specific intervals of wave numbers were selected to make the baselines, ensuring in this way that band overlapping in the whole cure process is avoided. All the FT-NIR experiments were repeated to ensure a good reproducibility of the results.

The fluorescence spectra were recorded in an Edinburgh fluorimeter using an optical fiber cable both for exciting and collecting the fluorescence. The fluorescent sample is located, as in the FT-NIR experiment, inside an oven between two microscope–glass slide plates. The excitation and emission slits were set at 2 and 5 mm, respectively, which correspond to a bandpass of 1.8 and 4.5 nm, respectively. All the spectra were recorded between 360 and 650 nm, setting the excitation wavelength at 340 nm and selecting a dwell time of 0.1 s and one scan. As in the case of FT-IR, the curing reaction was monitored at 50, 60, 70, and 80°C, controlling the temperature with the same SPECAC device.

Results and discussion

FT-NIR experiments

As an example, in Fig. 1, the evolution of the FT-NIR spectra for the DGEBA-DAMP reactive mixture (neat epoxy system) at 50°C is represented. For the other system studied (PMMA-modified epoxy) and the rest of the temperatures, similar results were obtained. The disappear-

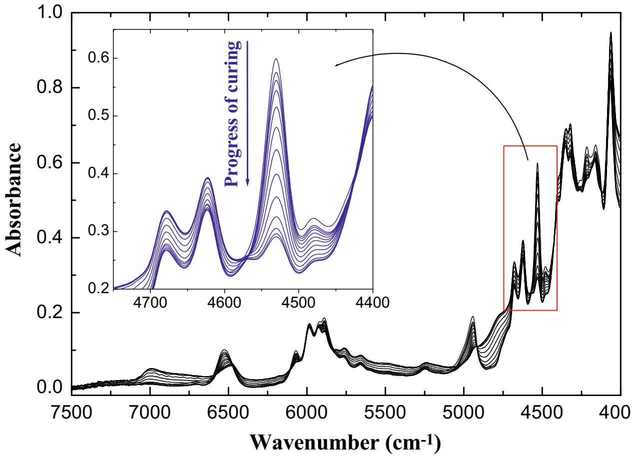

Fig. 1 Evolution of the FT-NIR spectra for the DGEBA–DAMP reactive mixture at 50°C

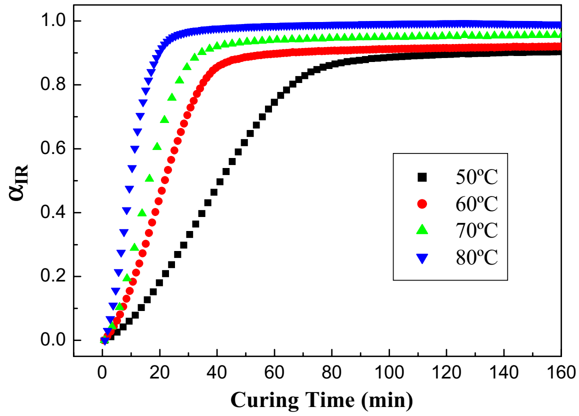

Fig. 2 Plots at different temperatures of the epoxy group conversion as a function of curing time for the PMMA-modified epoxy system

ance of the bands centered at 4,530 and 4,942 cm^{-1}, which usually are assigned respectively to (1) the overtone for the oxirane ring stretching mode and (2) the combination of the stretching and bending modes for the N–H in the primary amines [12, 13], is clearly observed.

The extent of reaction, α_{IR}, at any time *t* obtained from the FT-NIR spectra is calculated in terms of the epoxy group absorption according to Eq. (1):

$$\alpha_{\mathrm{IR}} = 1 - \frac{(\mathrm{A}_{\mathrm{E},t} \cdot \mathrm{A}_{\mathrm{R},0})}{(\mathrm{A}_{\mathrm{E},0} \cdot \mathrm{A}_{\mathrm{R},t})} \qquad (1)$$

where $A_{\mathrm{E},0}$ and $A_{\mathrm{R},0}$ refer to the initial areas of epoxy and reference bands, respectively, and $A_{\mathrm{E},t}$ and $A_{\mathrm{R},t}$ refer to their corresponding values at a given time *t*. The area of the band centered at 4,530 cm^{-1} was used to monitor the disappearance of the epoxy group, while the band at 4,623 cm^{-1} due to a combination band C–H stretching vibration of the benzene ring was used as reference [12, 13].

Figure 2 shows an example of the plots at different temperatures of the epoxy group conversion as a function of curing time for the PMMA-modified epoxy system. The sigmoidal profiles obtained are typical for the diepoxy–diamine cure reactions [12, 13, 15], indicating mainly three steps during the cure reaction: (1) the beginning of the reaction with a moderate reaction rate, (2) the autoacceleration part due to an increase of local concentration of the reactive groups and autocatalysis with a fast or relatively fast reaction rate, and (3) the region for which the reaction is diffusion-controlled, in which the mobility of the reactive groups is so restricted that when the reaction is nearly stopped, the reaction rate trends toward zero.

The curves obtained for the neat epoxy sample are similar to those of Fig. 2, although it was found, independently of temperature, that the evolution of epoxy conversion goes slightly faster and reaches a slightly higher value at infinite cure time when the epoxy system is modified with PMMA. This result is apparently opposite to the well-described dilution effect [17, 18, 36]. Considering the small amount of PMMA (2% w/w) in the modified epoxy system, the variation that might be expected in terms of the dilution effect should be within the experimental error associated to the FT-NIR sensibility and the uncertainties in the baselines; therefore, this effect should not be even observed.

A possible explanation of the results observed may be a change in the mechanism of the epoxy cure reaction. To see if there has been such a change under the effect of the PMMA, as an example, we have represented in Fig. 3 the dependence of the epoxy group concentration and the primary, secondary, and tertiary amino group concentrations in the reaction mixtures (neat and modified epoxy systems, respectively) on the curing time (*T*=50°C) according to the equations obtained from the mass balances described by Mikes et al. [15]. Similar results were obtained for the rest of the temperatures under study. The following findings can be outlined from Fig. 3, being possible to extract the same observations for the cure temperatures of 60, 70, and 80°C:

1. When PMMA-modified epoxy system is considered, the reaction of epoxy groups takes place slightly faster, and the final conversion is also slightly higher.
2. The curves for the evolution of the primary amino group concentration of both the neat epoxy system and the PMMA-modified epoxy system almost overlap.
3. There is an increase of the secondary amino group reaction rate when the epoxy system is modified with PMMA.
4. The final concentration that is reached at constant temperature of the tertiary amino groups is higher when the epoxy system is modified with PMMA.

The first observation might be due to the uncertainties in the calculation of the area bands in FT-NIR. However, the same observation can be done for the rest of the cure temperatures studied, giving a reproducible feature to the

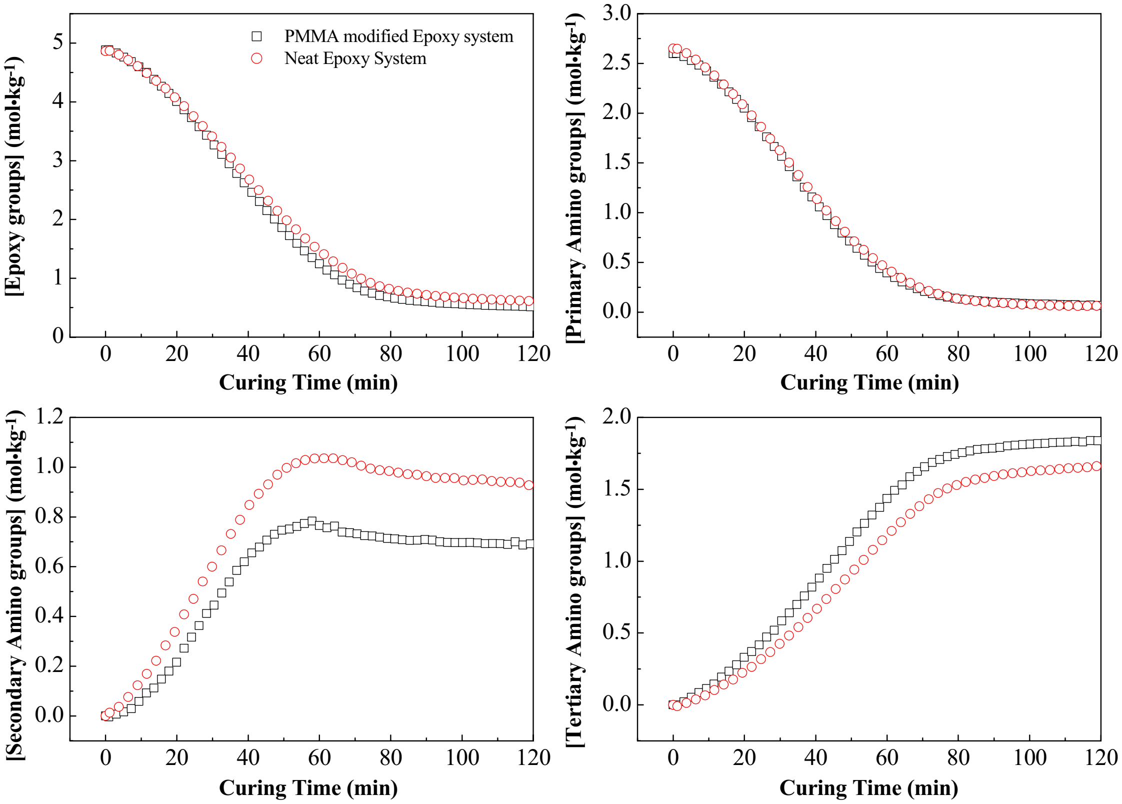

Fig. 3 Dependence of the primary, secondary, and tertiary amino group concentrations in the reaction mixtures (neat and modified epoxy system, respectively) on the curing time at 50°C

results. Besides, considering the resolution of the FT-NIR spectra (4 cm^{-1}), the maximum error associated to the determination of the band areas is about 15%, while the epoxy group concentration at the last stages of the curing process for the neat epoxy system is 20% higher than that of the PMMA-modified epoxy system. Therefore, the differences observed in Fig. 3 for the epoxy group reaction seem to be due to other reasons rather than simple uncertainties in the baseline selection for the band integration. On the other hand, the second observation is nearly in accordance with that expected in terms of the dilution effect; the primary amino group reaction rate almost does not change when the epoxy system is modified with such a low fraction of PMMA. Finally, observations 3 and 4 mentioned above would confirm that the presence of PMMA induces a small change in the mechanism of the epoxy cure reaction by means of an enhancement of the secondary amino group reactivity.

However, it would be interesting to study additionally the actual global effect of the PMMA in the DGEBA/DAMP reaction kinetics. To carry this out qualitatively, it is only necessary to calculate from the experimental data an apparent activation energy for the whole cure process with and without PMMA.

Probably, the simplest kinetic analysis to obtain apparent activation energies is to use an isoconversional method [31]. Representing the natural logarithms of the curing time for a specific value of the epoxy group conversion, α_{IR}, vs the inverse of cure temperature in kelvin, straight lines should be obtained, and from their slopes, apparent activation energies should be able to be calculated as stated in [31]. The values obtained with this method for the apparent activation energies, E_a, of the samples under study, the neat epoxy system and the PMMA-modified epoxy system, were 11.1±0.7 and 10.3±1.0 kcal·mol^{-1}. Therefore, considering the error, it seems that the addition of PMMA, at least at such small amount of 2% w/w and using this method of analysis, does not exert any appreciable effect in the whole kinetics of the chemical reaction epoxy–amine. However, the representation of the activation energies at several values of epoxy group conversion (those for which the isconversional method is a better approximation, Fig. 4) shows that the tendency for the PMMA-modified epoxy system is to have a lower global activation energy which would be in accordance with that mentioned about a higher reaction rate for the secondary amino groups.

Furthermore, from the epoxy group conversion plots (Fig. 2), it is possible to obtain other additional data such as the gel and an estimation of the vitrification times (*Gt* and *Vt*, respectively) since they can be very useful as parameters to control the cure process and because they will be neces-

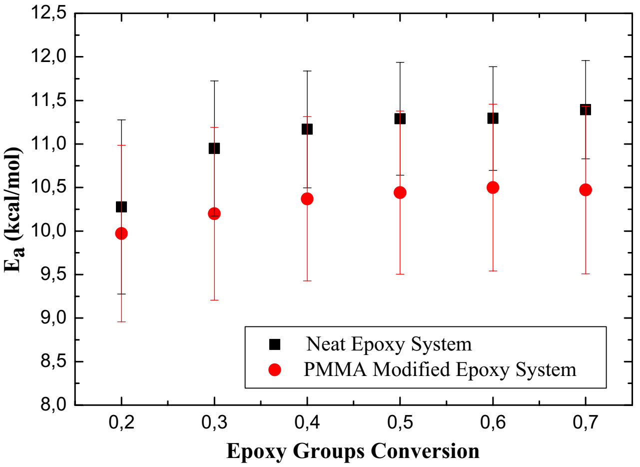

Fig. 4 Activation energies obtained at several values of epoxy group conversion for the neat and PMMA-modified epoxy systems

sary later for the analysis and interpretation of the data obtained with other experimental methods.

The gel times can be estimated from the epoxy group conversion plots (Fig. 2) as the times for which the extent of reaction is 0.588, according to the Flory–Stockmayer theory for diepoxy–diamine cure processes [37]. On the other hand, the beginning of the vitrification process has been considered as the time for which the reaction is clearly diffusion-controlled. The times for which the latter is happening have been taken as the values of time for which the epoxy group conversion plots (Fig. 2) start to level off (cross-point between two straight lines, one coming from the best fit in the part of the plot in which the reaction rate is the fastest and the other coming from the part of the plot in which the reaction rate is the slowest). However, much care should be taken into account with this consideration since the vitrification is related with the dynamics of the polymer, and other techniques would be more convenient for analyzing it, for instance, DMTA. Both the gel and these “pseudovitrification” times are gathered in Table 1.

FT-MIR experiments

As an example, we have shown in Fig. 5a several FT-MIR spectra of the epoxy–PMMA sample at 70°C and at different curing times (3.9, 6.4, 9.0, 11.5, 14.05, 16.6, 19.1, 21.7, 24.2, 26.7, 29.3, 31.8, and 34.3 min respectively). The typical evolution of an epoxy/amine mid-infrared spectrum is observed when the reaction progresses [38, 39]. There is a continuous decrease of both the oxirane ring absorption at 916 cm^{-1} and the absorbance due to the symmetric and antisymmetric stretching modes of the amino groups (3,316 and 3,381 cm^{-1}, respectively), while there is an increase of the absorption due to the stretching modes of the –O–H groups, which are created as the epoxy groups react with the amino groups. Thus, it should be possible to monitor the cure process from the evolution of those bands; however, that is not as accurate as in the case of using the bands in the near infrared range. The reason for that is a larger overlapping with other bands, which makes it more difficult to select an adequate baseline and, consequently, to obtain an accurate absorbance as a function of curing time.

On the other hand, in the case of the mid-infrared spectra, FT-MIR, the band assigned to the stretching mode of the carbonyl group for the PMMA component (1,734 cm^{-1}) is clearly observed. When the part of the spectra in which this carbonyl band is located is enlarged (Fig. 5b), a very slight shift as a function of curing time is observed. In fact, this shift is so weak (as expected, considering the small amount of PMMA in the mixture) that it is even lower than the resolution used to obtain the spectra. However, the shift can be analyzed in terms of the ratio of absorbances at two different wave numbers, at least to have a qualitative vision of what is going on. On the other hand, this kind of analysis using relative data or averages usually allows improving the resolution in almost two orders of magnitude [29].

The appearance of a low energy contribution for the carbonyl band when hydrogen bonds occur [40–42] is very well known. Particularly, in the case of DGEBA/PMMA blends, Janarthanan and Thyagarajan [40] observed and

Table 1 Gel, vitrification, and reaction-induced phase separation times (see text)

Epoxy sample	*T* (°C)	Techniques and methods					
		FT-NIR		FT-MIR	Fluorescence		
		Gt (min)	*Vt* (min)	$t(A_{1,734}/A_{1,723})$ (min)	$t_{\mathrm{Intensity}}$ (min)	$t\langle\nu\rangle$ (min)	$Vt\langle\nu\rangle$ (min)
Neat	50	50	72	–	–	–	81
	60	28	41	–	–	–	51
	70	19	26	–	–	–	34
	80	11	16	–	–	–	25
PMMA-modified	50	47	68	43	48	52	93
	60	25	38	26	33	33	66
	70	19	27	17	22	25	49
	80	11	17	15	10	10	27

FT-NIR, *FT-MIR* Fourier transformed infrared spectroscopy (near and medium, respectively), *PMMA* poly(methyl methacrylate)

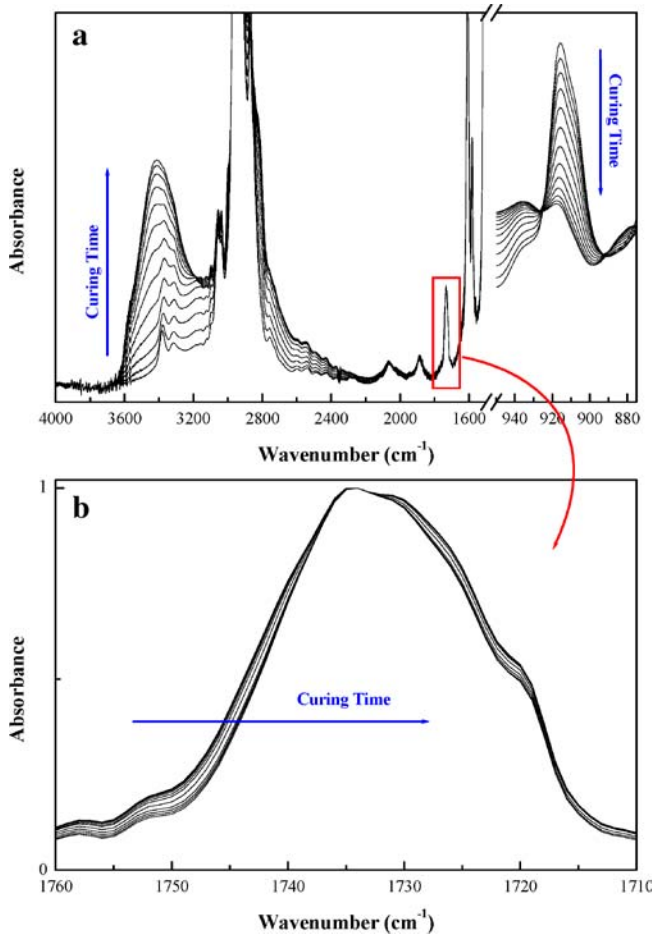

Fig. 5 FT-MIR spectra at different curing times of the epoxy–PMMA sample at 70°C. **a** Whole range. **b** Carbonyl band range

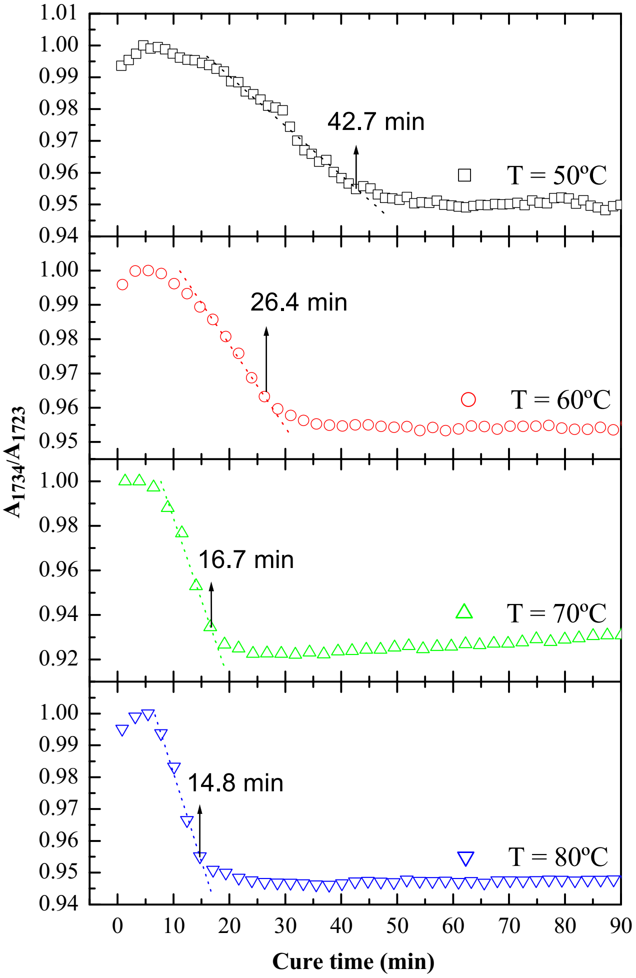

Fig. 6 Shift of the carbonyl band with curing time. Evolution of normalized ratio between the absorbance at 1,734 cm^{-1}, $A_{1,734}$, and the absorbance at 1,723 cm^{-1}, $A_{1,723}$

attributed the modification of the carbonyl absorption band to hydrogen bonding between the C═O groups of the PMMA and the hydroxyl groups of the epoxy component in an epoxy–amine reactive mixture. Besides, other authors consider the possibility of hydrogen bonding between the carbonyl groups and the amino groups [43]; however, these ones should exert a lower effect due to the lower electronegativity of the nitrogen in the amino groups with respect to the oxygen in the hydroxyl groups. Therefore, it is reasonable to think that the variation in the carbonyl band with curing time must be due to the hydroxyl appearance rather than to the primary and secondary amino group disappearance.

To see with more clarity the evolution (slight shift) of the carbonyl band as the cure progresses, we represented in Fig. 6 the normalized ratio between the absorbance at 1,734 cm^{-1}, $A_{1,734}$, and the absorbance at 1,723 cm^{-1}, $A_{1,723}$, vs curing time when the experiment is carried out at different temperatures (50, 60, 70, and 80°C). For all temperatures under study, two well-defined regions that at least ensured the qualitative analysis mentioned above are observed. In the first region, there is a fast decrease of the absorbance ratio, $A_{1,734}/A_{1,723}$, while in the second one, there is a very slow increase of the absorbance ratio. Taking into account that there must be an increase of the lower energy contribution to the carbonyl absorption band when the number of specific interactions by means of hydrogen bonds increases, the first region of the plots in Fig. 6 suggests that in that period of reaction, there is an homogeneous mixture, allowing therefore effective specific interactions between hydroxyl groups of the epoxy reaction mixture and the carbonyl groups of the PMMA. As the curing proceeds, the number of hydroxyl groups increases, and if no phase separation takes place, the lower energy contribution to the absorption band of the carbonyl groups should increase. However, if phase separation takes place, the additional hydroxyl groups created during the cure process should not have access to the carbonyl groups of the rich PMMA domains. Therefore, the point at which there is a clear change in the slope of $A_{1,734}/A_{1,723}$ (Fig. 6) should indicate the time at which there is, at a molecular scale, an incipient phase separation.

Figure 6 and Table 1 show the cure time obtained from the onset of the changes (from negative to positive slope) in the FT-MIR plots at which phase separation occurs at four temperatures, $t(A_{1,734}/A_{1,723})$. It is observed that these phase separation times are near the values of gel times obtained (Table 1), taking the value of gel conversion, 0.588, given by the Flory–Stockmayer theory for diepoxy–diamine cure processes [38]. This near coincidence suggests therefore that the very low fraction of PMMA (2% w/w) and its favorable interactions with the epoxy system allow a relatively large window of miscibility with respect to the epoxy conversion.

Steady-state fluorescence experiments

As an example, the evolution of the dansyl fluorescence spectra for the PMMA-modified DGEBA–DAMP reactive mixture at 50°C is shown in Fig. 7. For the neat epoxy system and the rest of the temperatures under study, similar results were obtained.

Two phenomena can be clearly observed in the spectra of Fig. 7 as the cure reaction progresses: (1) an increase of the fluorescence intensity and (2) a blue shift of the fluorescence band. Assuming that, in this system, only two photophysical phenomena account for the deactivation of the excited state of the dansyl chromophore, fluorescence and thermal deactivation by collisions (other photophysical phenomena such as quenching, nonradiative energy transfer, cross-system, etc., are considered negligible), an enhancement of the fluorescence intensity as polymerization advances is usually explained by an increase of the viscosity [20, 21, 28–31, 33, 34].

Throughout any polymerization process, there is an increase of the average molecular weight of the reactive species, which implies a reduction of their mobility and, therefore, an enhancement of the viscosity of the reactive system. This reduction in the mobility of the reactive species makes their collisions with the dansyl chromophore in its excited state more difficult to be deactivated nonradiatively. If less nonradiative deactivation of the dansyl excited state occurs, the fluorescence quantum yield should increase and, consequently, the fluorescence intensity.

On the other hand, the dansyl moiety is one of those fluorophores showing solvatochromism [44]. It presents red or blue shift under the influence of the surrounding molecules of the solvent in which the dansyl is immersed. The excited state of the dansyl chromophore has a higher dipolar moment than that of the ground state. Therefore, after excitation, there is a reorientation of the solvent molecules around the dansyl groups due to the influence of the electric field created by the dipole of the dansyl excited state. This dipolar coupling yields stabilization of the excited state of the dansyl which should yield a fluorescence of lower energy (red shift), with its effectiveness dependent of the dielectric constant, refraction index (polarizability), and the time required for the solvent molecules to reorient with respect to the dipole of the dansyl excited state (viscosity) [44]. Therefore, if the solvent relaxation time is lower than the lifetime of the excited state, an increase of

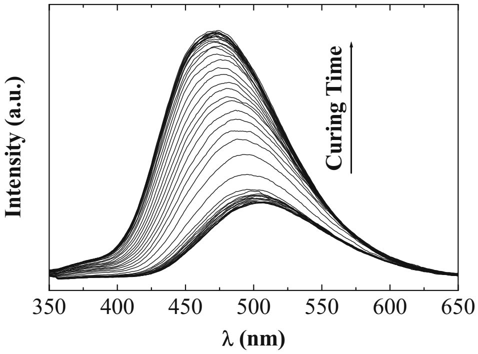

Fig. 7 Steady-state fluorescence spectra at different curing times of dansyl-labeled PMMA-modified epoxy (DGEBA-DAMP) at 50°C

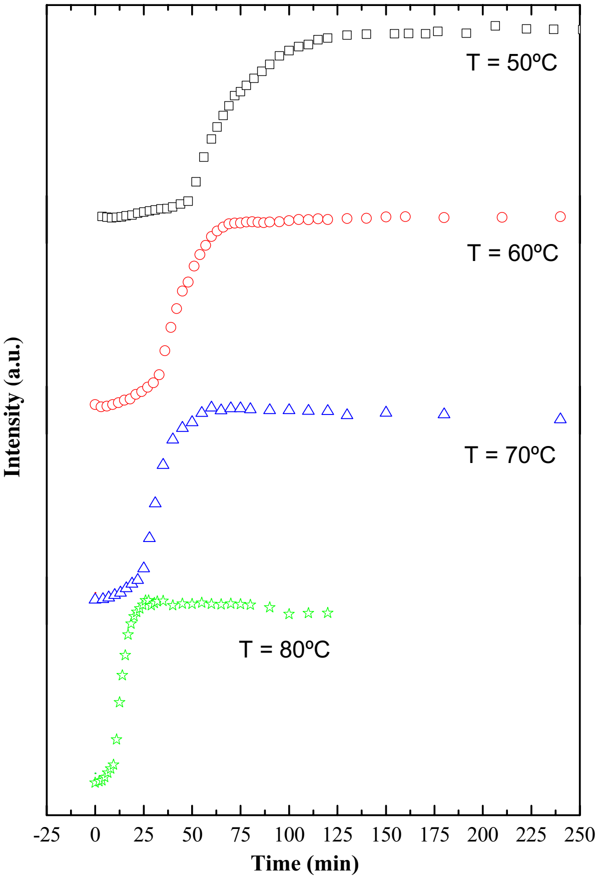

Fig. 8 Fluorescence integrated intensity as a function of curing time for the PMMA-modified epoxy system at different temperatures

the solvent polarity and/or polarizability should yield a red shift.

As infrared spectra show the bands at 6,000 cm^{-1} (Fig. 3) and 3,400 cm^{-1} (Fig. 5), respectively, there is an increase of the hydroxyl groups with the epoxy curing. Therefore, the cure process implies the creation of very polar groups (–OH) whose coupling with the excited state of the dansyl should shift its fluorescence to lower energies. However, as can be seen in Fig. 7, there is a blue shift as curing proceeds. This result can be explained considering that the reduction of solvent relaxation time is higher than any possible increase of solvent polarity. However, it is interesting to highlight that the evolution of the fluorescence band arises from a balance of two effects, one is due to chemical changes of the system and the other is due to physical changes of the system; therefore, following the fluorescence of the systems under study as a function curing is a way to monitor the cure process in a general sense, not only accounting for the chemical changes as in the case of using FT-IR.

The fluorescence integrated intensity as a function of curing time for the PMMA-modified epoxy system at different temperatures is represented in Fig. 8. In all cases, including the neat epoxy sample (Fig. 9) and independently of temperature, similar profiles showing three main regions are observed:

1. At the first stages of the cure process, there is a slow increase of the integrated fluorescence intensity.
2. Suddenly, there is a fast increase of the fluorescence intensity.
3. Finally, at a certain time, the integrated fluorescence intensity levels off or even starts decreasing, slightly depending on the temperature.

Taking into account that during the cure reaction an increase of the fluorescence intensity is mainly due to an increase of the viscosity, these three regions might correspond to the three regions shown in the FT-NIR results: (1) the beginning of the reaction, (2) the autoaceleration part, and (3) the vitrification. However, differently to the FT-NIR results (Fig. 2), the fluorescence intensity data (Fig. 8) for the PMMA-modified sample show a clear discontinuity at a certain curing time, $t_{\mathrm{Intensity}}$, between the first and the second regions. This observation suggests that just at the curing time $t_{\mathrm{Intensity}}$, when a new process is starting, infrared spectroscopy (near range) has not enough sensibility to detect fluorescence intensity. This new process might be the phase separation. To confirm this finding, we represented in Fig. 9 the integrated fluorescence intensity as a function of curing time for the neat and PMMA-modified epoxy systems, respectively. Although two curing temperatures (50 and 80°C) are considered in Fig. 9, similar results are obtained when 60 and 70°C are taken into account. It is clearly observed that the neat epoxy system does not present the clear discontinuity. Since the only difference between these two systems when the curing is taking place is the phase separation, it is reasonable to think that the clear

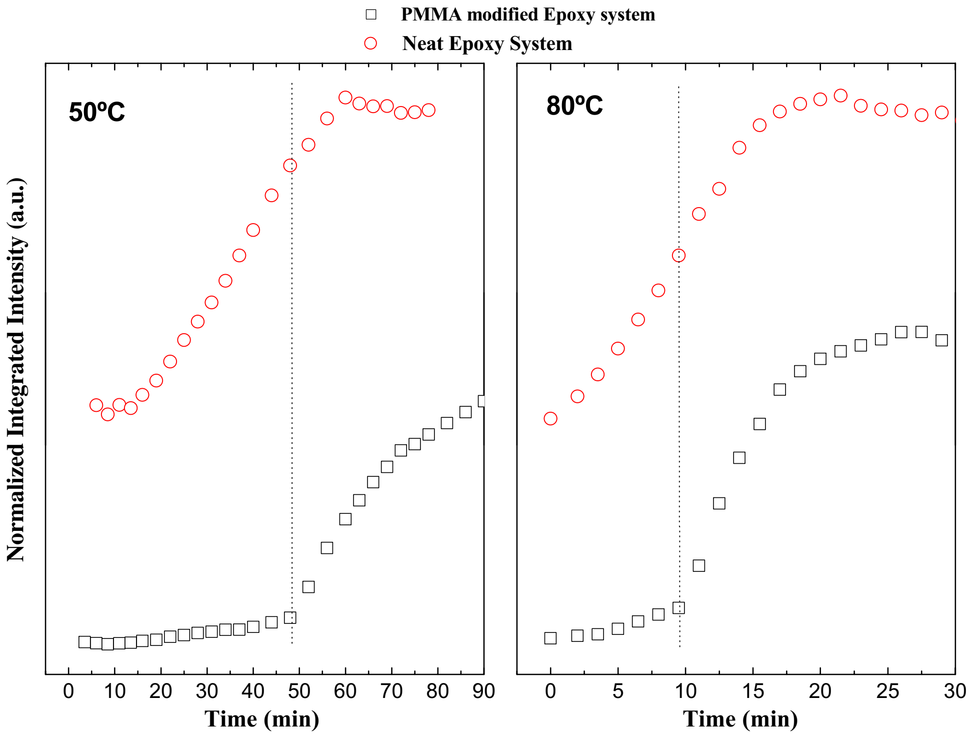

Fig. 9 Fluorescence integrated intensity as a function of curing time for the neat and PMMA-modified epoxy systems at 50 and 80°C

discontinuities observed in Fig. 8 are due to the incipient progress of that phenomenon.

When PMMA phase separates, the dilution effect that was assumed (although not observed by FT-NIR) and that was reported for other thermoplastic modified epoxy systems [17, 18, 36] disappears, and the reaction rate should increase. Probably, the reason why fluorescence intensity is sensible enough to this phenomenon may be that the reaction rate in terms of viscosity (reduction of nonradiative processes) increases faster than the chemical reaction rate. Furthermore, the fact that this discontinuity was absent in the neat epoxy sample supports the explanation given above. The values of curing time at which there is an important change in the increasing rate of the fluorescence intensity are grouped in Table 1 (Fig. 8). As can be seen, they are, although slightly higher, very close to those associated to phase separation obtained by FT-MIR. Probably, this small difference may be due to the criterion chosen (onset of the change) to obtain the phase separation time by FT-MIR (Fig. 6). This coincidence suggests again that following the fluorescence intensity changes of the dansyl chemically bonded to the epoxy component allows detecting the phase separation phenomenon quite easily.

We represented in Fig. 10 the first moment of the fluorescence band, ⟨ν⟩, as a function of curing time at four temperatures (50, 60, 70, and 80°C). The curves obtained for both the PMMA-modified epoxy sample and the neat epoxy sample are overlapped for comparison. A continuous increase of the first moment as a function of curing time with a kind of sigmoidal behavior as in the case of the evolution of fluorescence intensity (Fig. 8) and epoxy group conversion is observed for all curves (Fig. 2). Therefore, the same comments can be done in terms of the three parts of the cure process mentioned above. This continuous blue shift has been explained before as to be due to the most important contribution of the viscosity changes than to any possible change of the system polarity. Therefore, the curing time for which ⟨ν⟩ reaches a constant value should point to the glass state of the system since it indicates that there is no physicochemical change nearby the dansyl chromophore (at least in a timescale lower than the lifetime of the dansyl excited state, in nanoseconds). This observation allows one to estimate another vitrification time, but now in terms of the fluorescence data, *Vt*⟨ν⟩ (Table 1). In this case, the vitrification times have been taken as the values of time for which the ⟨ν⟩ plots (Fig. 10) start to level off. As can be seen in Table 1, the vitrification times obtained by fluorescence are always higher than those obtained by FT-NIR. This fact reveals that at the last stages of the curing, the fluorescence in terms of the first moment of the emission band is more sensible in monitoring the cure process for the systems under study. Furthermore, the

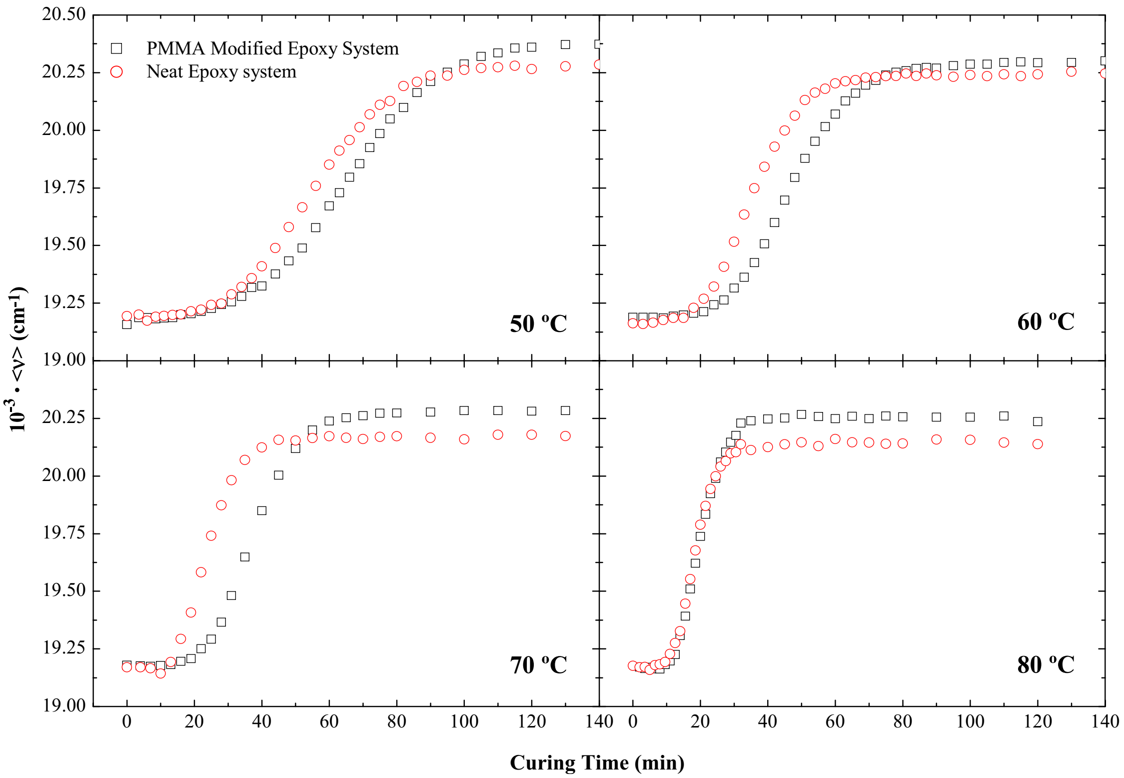

Fig. 10 Evolution of the first moment of the fluorescence band, ⟨ν⟩, with curing time at four temperatures (50, 60, 70, and 80°C)

vitrification times in terms of fluorescence for the PMMA-modified epoxy system are higher than those obtained for the neat epoxy system. This result suggests that the PMMA actually exerts a dilution effect, decreasing the reaction rate at least in a physicochemical sense.

On the other hand, independently of temperature, two more differences can be observed when comparing the results for the PMMA-modified epoxy sample and those obtained for the neat epoxy sample: (1) The first moment of the fluorescence band increases faster in the latter case, and (ii) the value of $\langle\nu\rangle$ reached for infinite cure time is slightly higher (~100 cm^{-1}) when PMMA is present in the epoxy mixture. The first observation may be again a clear indication of the dilution effect that could not be observed from the FT-NIR results. This result therefore points out that the dilution effect, at least for this system, is affecting the physicochemical changes of the modified epoxy system more exclusively than the chemical changes. This observation is really important to control adequately the processing during online manufacturing. The second observation may be indicative of two possibilities, when PMMA (2% w/w) is in the epoxy mixture: (1) the rigidity of the medium in which the dansyl moiety is immersed is higher, or (ii) the polarity of the medium in which the dansyl group is immersed is lower. The first possibility seems to be adequate if it is thought that the PMMA exerts a change in the mechanism of the epoxy curing, leading to a more cross-linked structure. In fact, this is completely in accordance with the FT-NIR results, which reveal that the concentration reached at constant temperature for infinite curing time of tertiary amino groups is always higher when the epoxy system is modified with PMMA. However, if one assumes that when the value of $\langle\nu\rangle$ levels off, the system has reached its glassy state, differences in rigidity should not be possible. The second possibility may be explained assuming that PMMA lowers the polarity by itself or because it compensates part of the polarity exerted by the hydroxyl groups when hydrogen bonds with the carbonyl groups occur at least nearby the dansyl chromophore.

Furthermore, comparing the values of $\langle\nu\rangle$ at infinite curing time for the different temperatures under study, it is observed that they decrease when the curing temperature increases. This result apparently is opposite to that expected, considering that the higher the temperature, the higher the conversion and, therefore, the higher the cross-link. However, it is necessary to take into account that the temperature is affecting the dynamics of the system and, therefore, the emission of the dansyl chromophore.

It is well known that, in general, for a dilute solution, any physicochemical property of it can be considered as the sum of the fractional contributions of that property for each component of the solution. Therefore, it can be assumed as a first approximation for this small amount of PMMA and in the case of a thermodynamically homogeneous mixture that the first moment of the dansyl fluorescence in the PMMA-modified epoxy system can be described by the equation:

$$\begin{aligned} < \nu >_{PMMA-Epoxy} = & \alpha_{Epoxy} < \nu >_{Epoxy} \\ & + \alpha_{PMMA} < \nu >_{PMMA} \end{aligned} \tag{2}$$

where α represents the fractional contribution of the first moment of dansyl group when immersed in the neat epoxy system, $\langle\nu\rangle_{\mathrm{Epoxy}}$, and in the PMMA, $\langle\nu\rangle_{\mathrm{PMMA}}$, respectively. The normalized coefficients, α_{PMMA} and α_{Epoxy}, can be given by:

$$\begin{aligned} \alpha_{PMMA} &= \frac{\omega_{PMMA}}{\omega_{PMMA} + K(1-\omega_{PMMA})} \\ \alpha_{Epoxy} &= \frac{K(1-\omega_{PMMA})}{\omega_{PMMA} + K(1-\omega_{PMMA})} \end{aligned} \tag{3}$$

where ω_{PMMA} is the weight fraction of the PMMA and K is a constant defining the component dependence of α_{PMMA} and α_{Epoxy}. Therefore, during the cure process, while the PMMA-modified epoxy system was a homogeneous mixture, the representation of the ratio $\langle\nu\rangle_{\mathrm{PMMA-Epoxy}}/\langle\nu\rangle_{\mathrm{Epoxy}}$ vs $1/\langle\nu\rangle_{\mathrm{epoxy}}$ should be a straight line, with slope and zero intercept of $\alpha_{\mathrm{PMMA}}\cdot\langle\nu\rangle_{\mathrm{PMMA}}$ (assuming a constant value for $\langle\nu\rangle_{\mathrm{PMMA}}$ if there is no reaction of the PMMA) and α_{Epoxy}, respectively. Just in the moment in which there is an incipient phase separation at a molecular scale, ω_{PMMA} and, consequently, ω_{Epoxy} should change, decreasing the former and increasing the latter. This effect therefore should be observed in the representation of $\langle\nu\rangle_{\mathrm{PMMA-Epoxy}}/\langle\nu\rangle_{\mathrm{Epoxy}}$ vs $1/\langle\nu\rangle_{\mathrm{epoxy}}$, which should decrease continuously its slope until reaching a constant value for the ratio $\langle\nu\rangle_{\mathrm{PMMA-Epoxy}}/\langle\nu\rangle_{\mathrm{Epoxy}}$.

We represented in Fig. 11 the values of the ratio $\langle\nu\rangle_{\mathrm{PMMA-Epoxy}}/\langle\nu\rangle_{\mathrm{Epoxy}}$ vs $1/\langle\nu\rangle_{\mathrm{epoxy}}$ at different curing times for four temperatures (50, 60, 70, and 80°C). A similar profile is observed in every case. At the beginning of the cure process, when the values of $\langle\nu\rangle$ are low, the points of the curves fit acceptably to the straight lines with positive slopes. This result therefore suggests that at a low epoxy conversion, Eq. (1) describes adequately the photophysical behavior of the dansyl group immersed in the PMMA-modified epoxy system. Furthermore, the plots of Fig. 11 show a minimum. This minimum appears for values of $\langle\nu\rangle$ during the cure process where the corresponding curing times, $t\langle\nu\rangle$, nearly coincide with those obtained by FT-MIR and integrated fluorescence intensity and that were assigned to the times when phase separation occurs (Table 1). As can be seen, the value of $\langle\nu\rangle$ for which the minimum appears is nearly the same for the cure temperatures 50, 60, and 70°C and clearly lower at 80°C. This result suggests that, at least for this system with this PMMA composition and for curing temperature lower than

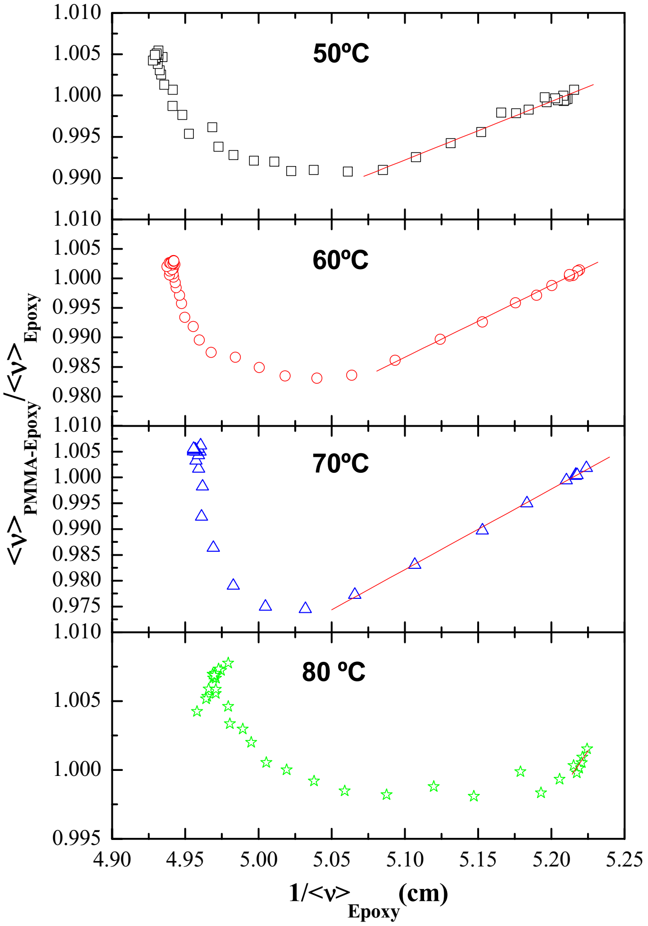

Fig. 11 Representation of the ratio $\langle\nu\rangle_{\mathrm{PMMA-Epoxy}}/\langle\nu\rangle_{\mathrm{Epoxy}}$ vs $1/\langle\nu\rangle_{\mathrm{epoxy}}$ at different curing times

70°C, the phase separation is mainly related to chemical or structural changes rather than dynamical changes of the system.

On the other hand, from the best linear fits after the minimum, it is possible to obtain the zero intercepts and, therefore, the values of K for each temperature. Furthermore, assuming that the value of K is constant during the whole phase separation process and considering that $\alpha_{\mathrm{PMMA}}$is negligible, from the value of the ratio $\langle\nu\rangle_{\mathrm{PMMA-Epoxy}}/\langle\nu\rangle_{\mathrm{Epoxy}}$ at the minimum, it would be possible to estimate the composition of the epoxy-rich phase (Table 2). Although for the temperatures 60 and 70°C the values of ω_{PMMA} are very close to the initial composition of the modified epoxy system (before curing), which obviously cannot be possible, as a first approximation, the data obtained are reasonably acceptable, and at least, they might be used in a qualitatively way. In general, it is observed how the amount of PMMA dissolved in the epoxy-rich phase increases when the cure temperature increases, except for 80°C, for which an important decrease in the amount of PMMA dissolved in the epoxy-rich phase after phase separation is observed. This result is completely in accordance with that stated by other authors about the competition between the dynamics (viscosity) of the system and the chemical reaction rate [5]. In the system under study, the composition of the separated phases seems to be controlled by the cure reaction rate. The data in Table 2 suggest that the faster the phase separation, the higher the temperature, until 70°C, and that the PMMA macromolecules have less time to diffuse to the PMMA-rich phase when the temperature is higher. On the other hand, from 80°C, the composition of the separated phases seems to be diffusion-controlled since the amount of PMMA in the epoxy-rich phase decreases when the temperature is high enough.

Table 2 Parameters obtained from the analysis of the curves in Fig. 9

T (°C)	Zero intercept	Slope· ($\times10^{-3}$ cm^{-1})	K	ω_{PMMA} after phase separation
50	0.63	7.08	0.0855	0.009
60	0.36	12.2	0.0423	0.017
70	0.19	15.6	0.0291	0.020
80	0.18	15.8	0.0285	0.002

After the minimum, while the first moment increases, the ratio $\langle\nu\rangle_{\mathrm{PMMA-Epoxy}}/\langle\nu\rangle_{\mathrm{Epoxy}}$ increases continuously. This behavior might be explained by a continuous increase of K as the cure progresses after the phase separation if the expressions (2) and (3) are still valid for the epoxy-rich phase in which the dansyl moiety is mainly immersed. This result suggests that K may include somehow the ratio between fluorescence quantum yields (the fluorescence quantum yield of the dansyl exclusively immersed in the epoxy mixture and in the PMMA, respectively). The values of those fluorescence quantum yields should show their highest changes at the gel point, as it happens, where the viscosity increases to infinite, leading therefore to the highest changes in the nonradiative processes. The fluorescence quantum yield depends inversely on the nonradiative constant rate and also on the medium in which the fluorophore is immersed; the higher the quantum yield, the lower the nonradiative processes to deactivate the excited state of the Dansyl fluorophore [44]. In fact, this consideration is in accordance with the dependence of the slope with the temperature in the linear region of the plots in Fig. 11 (Table 2) since the nonradiative constant rates for the dansyl in the epoxy and PMMA components must have different dependencies with the temperature. The energy required in each component (epoxy and PMMA) to allow the minimum polymer motion to deactivate the excited state of the dansyl group must be different because the dynamics of those polymers is different.

Comparison between FT-NIR and steady-state fluorescence

We represented in Fig. 12, for the two systems under study (PMMA-modified epoxy and neat epoxy systems), the first moment of the fluorescence emission band as a function of the epoxy group conversion obtained by FT-NIR at different temperatures. These curves were obtained by the corresponding extrapolations from the plots of FT-NIR epoxy group conversion, α_{IR}, vs curing time and the plots of the first moment of the fluorescence emission band, $\langle \nu \rangle$, vs curing time. As can be seen in both systems (PMMA-modified epoxy system and the neat epoxy system) and independently of temperature, there is no linear correlation between the evolution of chemical reaction in terms of the FT-NIR epoxy group conversion and the evolution of physicochemical changes in terms of the first moment of the emission band. It can be observed in two parts in each plot, one at low conversions with a very low slope and the other with higher slope (more than 92% higher) at higher conversions. These observations can be explained by taking into account that, with FT-NIR, a chemical reaction is followed; thus, higher changes in conversion are observed from the beginning until a specific conversion is reached, for which small changes in the chemical reaction will increase the viscosity of the system considerably. Therefore, FT-NIR seems to be more useful to follow the epoxy cure process during its first stages, while the steady-state fluorescence should be recommended to follow the cure processes at their last stages.

On the other hand, comparing the results obtained for the PMMA-modified sample with those of the neat epoxy system, it can be observed that the sharp increase of the first moment is delayed to higher chemical conversions when the epoxy system is modified with PMMA, at least for the composition under study. Furthermore, this delay increases as temperature increases from 50 to 70°C. This result suggests that the PMMA is acting as a kind of plasticizer during the cure process, which may increase the reaction rate of the secondary amines and delays the point (in terms of conversion) at which the reaction is being diffusion-controlled. In fact, this aspect is completely in accordance with the reactivity enhancement of the secondary amines observed by FT-NIR (Fig. 3). Furthermore, in the case of the PMMA-modified epoxy system at 80°C, the slope of the second region (Fig. 12a) clearly increases with respect to those obtained at the other temperatures. This result suggests again that at this temperature, during the phase separation process, the PMMA diffusion is faster, decreasing therefore the amount of PMMA in the epoxy-rich phase. This phenomenon should increase the curing rate because of a decrease of the dilution effect. Thus, the rigidity of the medium in which the dansyl is immersed should increase faster at 80°C as it is observed in Fig. 12a, by means of a faster increase of the first moment with conversion.

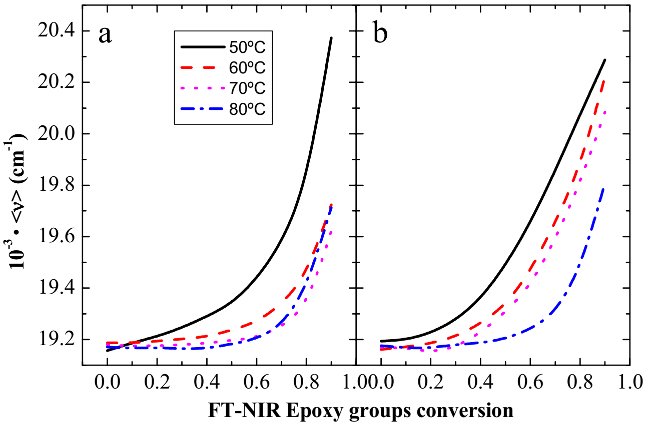

Fig. 12 First moment of the fluorescence emission band as a function of the epoxy group conversion obtained by FT-NIR at different temperatures. **a** PMMA-modified epoxy system. **b** Neat epoxy system

Conclusions

Fourier transformed infrared spectroscopy (near, FT-NIR, and medium, FT-MIR, ranges) and steady-state fluorescence spectroscopy were used to monitor the epoxy cure reaction and the induced phase separation in a PMMA (2% w/w)-modified diepoxy–diamine model system.

FT-NIR and fluorescence (by means of the first moment of the emission band) results suggest that the PMMA exerts a change in the mechanism of the epoxy cure reaction by means of an enhancement of the secondary amino group reactivity.

Following the spectral shift associated to the carbonyl band in the medium range of the infrared, it has been possible to monitor the phase separation process at a molecular scale.

The phase separation times obtained from different experiments are close to the values of gel time. This fact suggests that the very low fraction of PMMA (2% w/w) and its favorable interactions with the epoxy system allow a large window of miscibility with respect to the epoxy conversion.

The evolution of the fluorescence band of the dansyl group (chemically bonded to the epoxy component) seems to arise from a balance of two effects, one is due to chemical changes of the system and the other is due to the physical changes of the system. Therefore, following the fluorescence of the systems under study as a function of curing time is a way to monitor the cure process in a general sense, not only accounting for the chemical changes as in the case of using FT-NIR.

The intensity of fluorescence seems to be sensible enough to detect reaction-induced phase separations. Probably, the reason for this may be that the reaction rate in terms of viscosity (reduction of nonradiative processes) increases faster than the chemical reaction rate.

The fluorescence results in terms of the first moment of the emission band seem to point out that the dilution effect, at least for the system under study, is affecting the physicochemical changes of the modified epoxy system quite more exclusively than the chemical changes. This observation is really important to control adequately the processing during online manufacturing.

Furthermore, a theory to explain the behavior of the dansyl fluorescence during the curing of a thermoplastic/diepoxy–diamine blend showing a reaction-induced phase separation has been proposed. The model proposed from that theory fits quite well to the experimental data and also allows estimating the composition of the phases after nearly complete cure.

Finally, it has been demonstrated that FT-NIR and fluorescence spectroscopies are complementary techniques for proper monitoring of a cure process. FT-NIR seems to be more useful to follow the epoxy cure process during its first stages, while the steady-state fluorescence should be recommended to follow the cure processes at their last stages.

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