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ORIGINAL CONTRIBUTION

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Morphologic and kinetic study of an epoxy-poly(ethyleneoxide) system. The fluorescence to predict miscibility

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Abstract The kinetic of the curing process in the ethylenediamine (EDA)-poly (bisphenol A-*co*-epichlorohydrin) glycidyl end-capped (DGEBA) mixture modified with poly(ethylene oxide) (PEO) was studied. The epoxy component was labeled with a fluorescence group (dansyl) treating the DGEBA with the reactive dansyl derivative DNS-EDA. Dynamic DSC experiments were carried out and from their results the effect of the PEO composition on the epoxy curing was discussed. Furthermore, the effect of cure temperature and PEO composition on the morphology and crystallinity of the blend were studied as well. The morphologic study was carried out using complementarily optical transmission (TOM) and epifluorescence (EFM) microscopy. It was observed that: i) the addition of a non-reactive thermoplastic leads to a dilution effect of the reactive groups and therefore a decrease of the epoxy amine reaction rate; ii) the PEO composition does not seem to affect the non catalyzed process of the epoxy curing, while an increase in the PEO fraction within the epoxy/PEO mixture seems to change the mechanism of the cure reaction; iii) dynamic DSC scans, TOM and EFM images and steady state fluorescence spectra of the cured samples suggest that when the curing temperature increases there is an increase in the miscibility between PEO and the epoxy-amine reaction mixture; and iv) a reduction in the PEO/cured epoxy miscibility as the fraction of PEO increases was observed.

Keywords Epoxy · Poly (ethyleneoxide) · Fluorescence · Dansyl group

Introduction

One of the main objectives in the polymer field is to find new high performance materials. During the last years, as an alternative to polymer synthesis, there has been much work carried out with copolymers and blends trying to achieve specific synergetic effects. Everything can be mixed and is therefore susceptible of being studied. Particularly, the epoxy-based thermosets have been the objective of multiple modifications in order to increase mainly their toughness and to reduce their poor resistance to crack propagation. Most of the research related to this aspect has focused its attention on studying the effects of those modifications on curing, mechanical properties, etc. Generally, the epoxy based thermosets have been modified with thermoplastics such as poly(methylmethacrylate) [1, 2, 3], poly(ethersulfones) [4, 5], etc; elastomers, such as carboxyl terminated butadiene acrylonitrile [6, 7] and silicones [8]. However, few studies have been done with semicrystalline polymer modified epoxies [9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. These systems are potentially very interesting since, after preparing the blend, their properties can be easily changed by a specific thermal treatment. Additionally, controlling the degree of crystallinity and the miscibility between the semicrystalline polymer and the thermoset offers new perspectives to the polymer applications. For instance, the subsequent extraction of the crystalline polymer with a convenient solvent might give a crosslinked epoxy polymer with a distribution of pore sizes and shapes under control.

The effect of the hardener in the miscibility between an epoxy resin and a semicrystalline polymer was studied by Clark et al. [9] and Noshay and Robeson [10]. They studied the miscibility of the epoxy thermoset/poly(ϵ-caprolactone), PLC, blends cured with anhydride and amine, respectively. From those studies it can be shown that the different compatibility in the epoxy blends with the PLC is due to the presence of hydroxyl groups in the amine-cured system, which allows the possibility of hydrogen-bonding interaction with the ester groups of the PLC.

Quipeng et al. [11] investigated the role of crosslink density on the miscibility of an epoxy thermoset with PEO. They studied the epoxy thermoset/poly(ethylene oxide) (PEO) blend cured with an aliphatic amine (tetraethylenepentamine) and observed a phase separation as the cure progressed. They considered it to be due to the large change in the chemical and physical nature of the epoxy resin during the crosslink process.

The effect of the blend composition in the miscibility of the system was studied by Sixun et al. [15] investigating blends of 4,4′-diaminodiphenylmethane-crosslinked diglycidyl ether of bisphenol A/PEO. They observed, using DSC and DMA that the components of the blend were miscible at any composition. At the same time, a marked negative deviation from FOX equation was noticed for the blends and they explained it in terms of an incomplete curing reaction due to the dilution effect of PEO as an inactive diluent.

Woo et al. [18] investigated the cure behavior of epoxy based on diglycidyl ether of bisphenol A/PEO cured with 4,4′-diaminodiphenyl sulfone (DDS). The incorporation of the crystalline polymer was found to exert no alteration on the cure mechanism, which remained autocatalytic for all the epoxy/PEO mixtures as well as for the pure DGEBA. They concluded that the PEO component, being in a miscible state with epoxy/DDS throughout the cure, only acted as a diluent for the reactive DGEBA epoxy and DDS components.

Horng et al. [16] studied several cured systems based on PEO/DGEBA for which different hardeners were used. Using DDS (4,4′-diaminodiphenylsulfone) and piromellitic dianhydride (PMDA) a miscible phase was observed while, when an aliphatic amine (diethylene triamine) is used, the curing process led to phase separation. Apparently, different structures of hardeners let to different chain segments of the cured epoxy, which in turn could influence the ultimate phase morphology of cured PEO/epoxy solids. In addition to this, the cure temperature was found to exert no effects in the phase homogeneity.

Furthermore, Woo et al. [14] studied the relationships between the spherulite morphology and changes in the interactions between the miscible PEO and DGEBA/DDS epoxy system before and after cure. It was concluded that in uncured and cured PEO/DGEBA-DDS, there are different hydrogen-bonding interactions among the ether group of PEO, hydroxyl group in epoxy, and the amine group of DDS.

In spite of the work carried out up to now, the relation: epoxy curing conditions—blend composition—morphology—properties does not seem to be completely understood yet. Therefore, much more attention should be focused to solve this aspect.

Fluorimetry is a very sensible and non-destructive technique. Furthermore, the use of the fluorescent response from labels has become a very powerful tool to follow changes in their surroundings such as polarity and/or rigidity [14, 19, 20, 21, 22]. One of the fluorescent labels more used for this purpose is the dansyl chromophore [20, 21]. The incorporation of the dansyl moiety chemically attached to the epoxy resin with a concentration low enough as to consider it no to alter the epoxy properties may be a useful choice to study different sorts of interactions between the epoxy and a crystalline polymer blended with it. At the same time, the image analysis obtained from fluorescence microscopy should be a complementary source of information in order to understand the effect of the polymer network on the crystallization of the crystalline polymer.

On the other hand, the kinetics of curing processes in epoxy systems must be known in order to optimize the final structure of these materials. This is the reason why the effect of the thermoplastic polymers incorporation in the epoxy reaction mixture has been the aim of many studies. It is well known that polymeric additives may affect the epoxy cure progress [18]. This situation is mainly expected for homogeneous-phase polymer/epoxy systems when the polymer remains soluble in the epoxy before and after crosslinking; for instance, by affecting: i) the reactivity of the epoxy and amine groups and ii) the viscosity of the reactive mixture. The later aspect may modify the diffusion control region of these kind of curing processes.

In this work, the cure kinetic of an ethylenediamine (EDA)-DGEBA mixture modified with PEO is to be studied. In order to do this, dynamic DSC experiments will be used and the effect of the PEO composition on the epoxy curing will be discussed. In addition to this, the effect of the cure temperature and the PEO composition on the morphology and the crystallinity of the blend will be studied as well. The morphologic study will be carried out using complementarily optical transmission and epifluorescence microscopy.

Experimental

Materials Poly(ethylene oxide) (PEO) supplied by Polymer Science, Inc. and $M_w = 6\times10^5$ g/mol was used as received. The melting point is $T_m = 63.1$ °C and the glass transition temperature, $T_g = -51.35$ °C. 5-Dimethylamino-1-naphthalenesulfonyl chloride (DNS), I, were supplied by Lancaster INC. The epoxy component, poly(bisphenol A-*co*-epichlorohydrin) glycidyl end-capped (DGEBA), II, $M_n = 348$ g/mol and the hardener ethylenediamine (EDA), III, were purchased from Aldrich Co.

Sample preparation The epoxy component was labeled with the dansyl fluorescent group treating the DGEBA with the reactive DNS derivative DNS-EDA, IV, following the procedure already described [23]. The concentration for the dansyl group was 5×10^{-4} mol/kg of epoxy mixture. With such a low concentration it is ensured that there is not any modification of the general properties of the system.

Different mixtures of PEO/DGEBA-EDA with the compositions 10 wt%, 20 wt% and 30 wt% of PEO were prepared as follows: the PEO was mixed with DGEBA at a temperature well above the PEO melting point (100 °C). The curing agent EDA was then added into the liquid mixture, and mechanically stirred for less than 2 min before subjecting the sample to the selected curing conditions. Six temperatures of curing were investigated: 70, 80, 90, 100, 120 and 140 °C. The cure processes were carried out for 3.5 h.

An amine-H/epoxy stoichiometry higher than 1 (1.5) based on the results of Zheng Sixun et al. [15] was chosen. They obtained the higher value of T_g for their PEO/DGEBA-DDM system in the amine excess region.

DSC measurements The thermograms of the curing processes were performed using a Mettler Toledo 12E differential scanning calorimeter, scanning from 25 to 220 °C with different heating rates (5, 10, 15, 20 and 25 °C/min), in a nitrogen atmosphere. Runs were carried out using an empty aluminum cell as the reference. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. These data were processed further to obtain the fractional conversion, $\alpha = \Delta H_t/\Delta H_0$, and the rate of reaction, $d\alpha/dt$, where ΔH_t is the area of the exotherm curve at time, t, and ΔH_0 the total area under the exotherm, based on the extrapolated baseline at the end of the reaction. Furthermore, the thermal transitions for the cured samples under specific conditions (thermal treatment and PEO/Epoxy composition) were determined. In every case, the cured samples were heated at 80 °C for 10 min and after that they were annealed at 50 °C for 1 h; finally, the samples were rapidly cooled at room temperature for at least 1 h. Thus, the same thermal history is ensured for all samples. After this treatment, DSC dynamic scans were carried out from −80 to 200 °C at 20 °C/min and the analysis of the DSC traces allowed us to obtain the melting point, T_m, and the glass transition temperature, T_g.

Optical transmission and epifluorescence microscopy In order to observe the morphology of the cured samples a Nikon Labphot, in both, the transmission (TOM) and the epifluorescence (EFM) modes, was used. To excite the sample in the EFM mode, an arc lamp of Hg was used, making the beam pass through a band filter of 330–380 nm. This spectral region corresponds to the maximum excitation for the dansyl group. The fluorescence emission is passed, by means of a dichroic mirror, through a cut filter at 420 nm in order to eliminate as much as possible the scattered light from the sample. In both modes of operation, TOM and EFM, the images of the morphologies were captured with a Nikon F601 camera.

Steady state fluorescence Using an Edinburg fluorimeter, fluorescence spectra were recorded for the cured samples (30% of PEO) at different temperatures (70, 80, 90, 100, 120 and 140 °C). The excitation and emission slits were 2.3 and 3.6 nm respectively, the dwell time was set at 0.2 ns, the excitation wavelength was 350 nm, two scans were carried out and an optical fiber cable to excite and collect "in situ" the fluorescence was used.

Results and discussion

DSC

In Fig. 1 typical thermograms for the curing, at different heating rates, of one of the samples under study (20% of PEO) are presented. The rest of the samples showed similar DSC traces.

The main data that can be extracted from the thermograms (initial and final cure temperatures, T_i and T_f, the temperature at the maximum cure rate, T_p, and ΔH_0) are grouped in Table 1.

In the fifth column, the numbers in brackets correspond to the exothermic enthalpy per gram of DGEBA-EDA mixture. All these values are very close each other, indicating that the stoichiometry remains constant for every sample prepared and may be the indication of a good sample preparation. Furthermore, in the last column the enthalpies of the epoxy-amine reaction per epoxy equivalent (ee) are shown. In every case the value obtained is very close to those given in the literature for epoxy-amine reaction systems, 98–111 kJ/ee [24, 25].

On the other hand, independent of the heating rate, the higher the proportion of PEO in the mixtures the

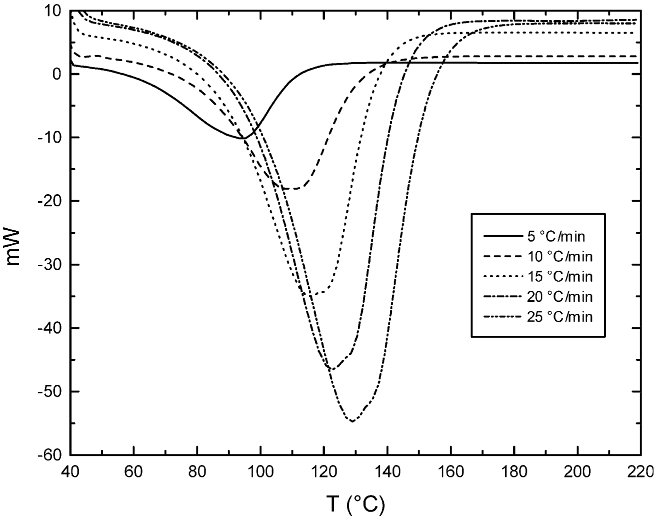

Fig. 1 Thermograms for the curing of one of the samples under study (20 wt% of PEO) at different heating rates

higher value of T_p, and therefore, the lower the epoxy-amine reaction rate. As was expected, the addition of a non-reactive thermoplastic provokes a dilution effect of the reactive groups and, therefore, a decrease of the epoxy-amine reaction rate [2, 16]. Besides, this result suggests that if the polymerization had induced phase separation in the amorphous state, it should have been quite small [26] since the dilution effect should not have any sense in the DGEBA-EDA domains.

From the fractional conversion, α, as a function of time and temperature, and from T_p data, it is possible to carry out easy kinetic analysis in which it is considered that DGEBA-EDA cure reaction proceeds via a global mechanism. These studies were done using common methods found in the literature.

Method I [27]

In this method it is assumed the autocatalytic (epoxy-amine-hydroxyl) contribution is negligible at high temperatures due to the difficulty of forming ternary complexes and, similarly, the reactivity of the primary and secondary amine hydrogens. Therefore, considering an Arrhenius like constant rate, the classic Hori's equation [28] can be transformed into

$$\ln\left[\frac{d\alpha/dt}{(1-\alpha)(r-\alpha)}\right] = \ln A - \frac{E_a}{RT} \tag{1}$$

where r is the amine/epoxy stoichiometric ratio, E_a is the apparent activation energy for the non catalyzed process, A the frequency factor, R the general gas constant and T the absolute temperature.

Therefore, by plotting the left part of Eq. (1) vs 1/T, a straight line should be obtained, whose slope would lead to the estimation of E_a for the non catalyzed process (Table 2).

Method II—Kissinger's method [29]

The Kissinger's method extended to the general case, can be expressed as

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \tag{2}$$

Differentiating α and T in Eq. (2) with respect to the time, t, results in

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = -\frac{E_a\beta}{RT^2} + A \cdot f'(\alpha) \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where β is the DSC scanning rate (°C/s). Equation(3) becomes zero at the maximum rate, and therefore

Table 1 Main data taken from the DSC thermograms for the cure process in the different systems under study. Initial and final cure temperatures, T_i and T_f, temperature at the maximum cure rate, T_p, and ΔH_0

Heating rate (°C/min)	T_i (°C)	T_f (°C)	T_p(°C)	ΔH_0 (J/g)	ΔH_0 (kJ/ee)
30% PEO					
25	62	206	138.7	428(611)	106
20	62	214	133.6	416(594)	103
15	50	170	126.5	423(604)	105
10	47	165	115.0	418(597)	104
5	44	141	97.3	427(610)	106
20% PEO					
25	53	192	129.1	498(622)	108
20	46	179	122.7	515(644)	112
15	43	173	115.7	508(635)	110
10	43	175	108.1	456(570)	99
5	40	139	94.2	493(616)	107
10% PEO					
25	40	189	124.0	574(638)	111
20	44	184	119.5	547(608)	106
15	41	186	113.4	508(564)	98
10	37	155	103.9	587(653)	114
5	35	139	91.6	577(641)	111

Table 2 Kinetic data obtained from the methods described in the text for three different compositions in the mixture PEO/DGEBA-EDA

Method	E_a (kJ/mol)		
	PEO 10%	PEO 20%	PEO 30%
Method I	88 ± 4	92 ± 3	92 ± 2
Method II	53 ± 1	51 ± 2	42 ± 1
Method III	49 ± 3	46 ± 3	40 ± 2

$$\frac{E_a\beta}{RT_p^2} = A\cdot[f'(\alpha)]\cdot\exp\left(-\frac{E_a}{RT_p}\right) \tag{4}$$

where T_p is the temperature at the maximum curing rate. Equation (4) is linearized by means of Eq. (5):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \left\{\ln R - LnE_a + \ln[f'(\alpha)]_p + \ln A\right\} - \frac{E_a}{RT_p} \tag{5}$$

For all the samples and heating rates studied, the value of $[f'(\alpha)]_p$ was nearly constant. In Fig. 2 this estimation is shown for one of the compositions as an example. The value of α at T_p is also independent of the heating rate. Therefore, if the value of $[f'(\alpha)]_p$ is constant, the plot of Ln (β/T_p^2) vs $1/T_p$ should be a straight line from whose slope a global activation energy could be obtained (Table 2).

Method III—isoconversional method [30]

The activation energy can be also determined by using the logarithmic form of the general kinetic equation, $\frac{d\alpha}{dt} = k(T)\cdot f(\alpha)$:

$$\ln\frac{d\alpha}{dt} = \ln[A\cdot f(\alpha)] - \frac{E_a}{RT} \tag{6}$$

where k(T) is the classical constant rate which only depends on the temperature under Arrhenius behavior, and f(α) is a function that only depends on the fractional conversion α.

After representing ln(dα/dt) vs 1/T at one specific value of conversion, an apparent activation energy, Ea, can be obtained (Table 2). The kinetic data obtained from all these methods are summarized in Table 2.

The error in method III was calculated using the values of E_a obtained for the different values of conversion considered (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8). The small uncertainty obtained, ~3 kJ/mol, may be an indication that the mechanism does not change with conversion.

Method I does not fit well the values of conversion at high temperatures as expected. Methods II and III fitted the experimental data quite well showing correlation, r, higher than 0.98. The data in Table 2 show that method I yields the higher values of E_a, being independent of the PEO fraction in the epoxy-PEO mixtures studied. On the other hand, methods II and III yield lower values of E_a in close agreement, although with slightly lower values, with those estimated by Horie et al. [28] (53.9 kJ/mol) and by Varma [31] (56 kJ/mol) for the pure DGEBA-EDA system determined by DSC. Furthermore, the values of E_a decrease when the PEO proportion increases in the Epoxy-PEO mixtures.

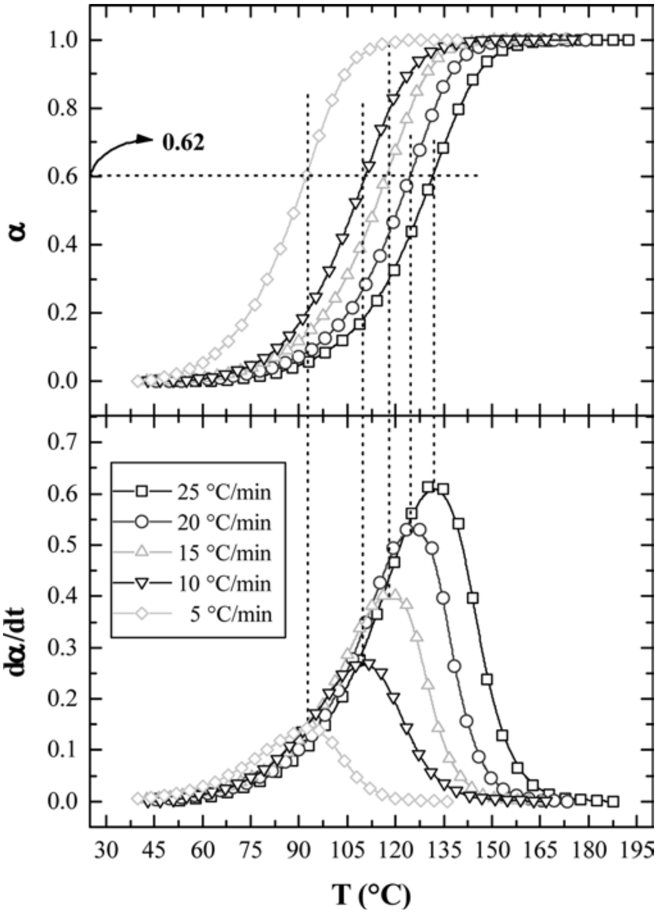

Fig. 2 Estimation of α at the maximum curing rate (at T_p). Sample with 20% of PEO

In the first method it is considered that the reaction takes place through a non-catalyzed mechanism and does not take into account the curing process at high conversions (high temperatures). On the other hand, methods II and III do not consider any specific mechanism. Therefore, the apparent activation energy in methods II and III should contain information from the whole process; in other words, information from any mechanism is independent of whether the reaction takes place by means of i) the catalyzed and/or non-catalyzed reaction or ii) a multimechanism process (chemical control and diffusion control). The fact that no variations in E_a were observed using the first method suggests that the PEO composition does not seem to affect the non-catalyzed process. This explanation and the results obtained with methods II and III seem to reflect that an increase in the PEO fraction within the epoxy/PEO mixture implies a more effective catalysis. The influence of the -OH groups from the PEO may be an explanation of the additional catalytic effect. This was the argument proposed by E.M. Woo et al. [32] to explain that the initial cure reaction rates of a phenoxy-modified epoxy were comparatively higher than those of the pure epoxy. They suggested that the -OH group in the phenoxy chains exerts a catalytic effect for the epoxide opening. However, taking into account the molecular weight of the PEO used, the concentration of the -OH groups does not seem to be high enough to exert any appreciable catalytic effect.

It is well known that the curing of epoxy-amine thermoset systems reaches a certain conversion for which the process is diffusion controlled. Accepting, at least, partial miscibility between the epoxy-amine system and the PEO, as the dilution effect suggests, another consequence of this effect may be a delay of the diffusion controlled process for the curing because of an increase of the free volume of the blend. This effect would allow the reactive groups to diffuse more easily to reach each other decreasing the apparent activation energy of the process. Therefore, the variation in the apparent activation energy as the fraction of PEO increases seems to be due to a change in the mechanism of the cure reaction rather than to changes in the catalytic effect.

Tables 3 and 4 show the data obtained from dynamic DSC scan for the fully cured samples; therefore those related to the crystallinity and the thermal transitions: enthalpy of fusion, ΔH_f, the melting point, T_m, the glass transition temperature, T_g (infection point), and the degree of crystallinity in terms of X_c(blend) and X_c(PEO) are calculated from

$$X_c(blend) = \frac{\Delta H_f(blend)}{\Delta H_f^0} \tag{7}$$

$$X_c(PEO) = \frac{\Delta H_f}{\Delta H_f^0} \tag{8}$$

where, ΔH_f(blend) and ΔH_f are the apparent enthalpies of fusion per gram of blend and PEO respectively, and $\Delta H_f^0 = 197$ J/g is the heat of fusion of 100% crystalline PEO obtained as an average from literature values [33, 34].

In all cases only one T_g was detected under the sensitivity of the DSC used, suggesting a certain level of miscibility between the PEO and the epoxy. In Table 3 the variations of these parameters as a function of curing temperature are presented when a 30 wt% of PEO was used in the mixture.

Although small variations in the thermograms can be observed when selecting the base lines, the data in Table 3 seem to reflect a specific trend. The fraction of PEO crystals and the value of T_g slightly increase when the curing temperature decreases. This result suggests that when the curing temperature increases the miscibility is improved (in the amorphous state) between PEO and the epoxy-amine reaction mixture. First of all, if the miscibility is higher, it is reasonable to think that the PEO will have more difficulty in acquiring the order associated with its crystalline phase because it will be more dispersed when interacting with the epoxy component. Besides, more compatibility between the epoxy and the PEO means that the PEO chains will surround more easily the epoxy chains causing therefore the experimental T_g to be closer to that predicted by an ideal system.

Among the expressions that relates the T_g of the ideal mixture with its composition, the Fox equation is very well known. The fifth column in Table 3 shows the values of T_gs calculated for the system under study using the Fox equation. As can be seen, the experimental data show a positive deviation which decreases with the temperature used for curing. Nevertheless, it is necessary to take into account that the weight fraction of PEO in the amorphous phase, W′(PEO), is not equal to the overall weight fraction of PEO in the blend, W(PEO). These quantities are related as follows:

$$W'(PEO) = (W(PEO) - X_c(blend))/(1 - X_c(blend)) \tag{9}$$

Recalculating the T_gs from the Fox's equation using the weight fraction of PEO in the amorphous phase, T_g', it can be observed (Table 3) that the positive deviation aspect to the experimental values of the T_g is not so important. Therefore, the reduction in the T_g of the cured blends seems to arise from a plasticization effect when important miscibility between PEO and epoxy exists in the amorphous state.

In Table 4, the results obtained from the study of the crystallinity variation and the thermal transitions as a function of the PEO-epoxy composition are presented. As expected, when the PEO fraction increases, the degree of crystallinity increases. Furthermore, the higher the PEO fraction the lower the glass transition temperature (Table 4).

Table 3 Enthalpy of fusion, ΔH_f, melting point, T_m, and glass transition temperature, T_g (inflection point) as a function of curing temperature. Samples with 30 wt% of PEO

Curing temperature (°C)	ΔH_f (J/g of PEO)	T_m (°C)	T_g (°C)	T_g (°C)	Fox T_g' (°C)	Fox X_c (blend) (%)	X_c (PEO) (%)
70	149.8	65	94	43.7	90.2	23	76
100	144.9	66	91		87.2	22	74
140	134.4	66	87		81.7	20	68

Table 4 Enthalpy of fusion, ΔH_f, melting point, T_m, and glass transition temperature, experimental, T_g(inflection point) and ideal (Fox equation) as a function of composition. Samples cured at 100 °C

W(PEO) (%)	W′(PEO) (%)	ΔH_f (J/g of PEO)	T_m (°C)	T_g (°C)	T_g (°C) Fox	T_g' (°C) Fox	X_c(blend) (%)	X_c(PEO)
0	0	-	-	115	115	115	-	-
10	6.6	71.71	64	110	87.9	96.7	3.6	36
20	7.1	137.1	66	104	64.4	95.5	14	70
30	10.2	144.9	66	91.4	43.7	87.2	22	74
100	100	157.9	63	-51.4	-51.4	-51.4	-	80

In order to analyze the compatibility of the mixture of polymers, the experimental variation of the T_g as function of the composition is usually compared with the same variation obtained from an ideal compatible system (Fox equation). The sixth column in Table 4 shows the values of T_gs calculated for the system under study using the Fox equation. As can be seen, the experimental data show a positive deviation which increases with PEO content. The phenomenon may be ascribed to a reduction of compatibility as the fraction of PEO increases. Nevertheless, it is necessary to take into account again the weight fraction of PEO in the amorphous phase, W′(PEO) (Eq. 9).

Recalculating the T_gs from the Fox's equation using W′(PEO), T_g', it can be observed (Table 4) that the positive deviation aspect of the experimental values of T_g is low and decreases when the PEO fraction increases. The later observation may be an indication of more compatibility when the PEO fraction increases, at least in the range of compositions studied.

Morphology

Figure 3 shows the optical transmission (left) and epifluorescence (right) images corresponding to the morphologies of the PEO/epoxy (PEO 30 wt%) cured at different temperatures: 70, 100 and 140 °C respectively. The cured samples were heated at 80 °C for 10 min and after that they were annealed at 50 °C for 1 h; finally, they were rapidly cooled down at room temperature. All the optical transmission images show a spherulitic morphology that is generated from a kind of dendritic nucleus. However, the morphology of the spherulites depends on the cure temperature.

The observed images suggest that the lower temperature of the epoxy curing the larger open zones between the fibrils. Although there is not complete miscibility between the PEO and the epoxy network (more than 30% of the PEO in the mixture) at room temperature, the homogeneous morphology observed (without any kind of domains) in the mixtures at the curing temperatures suggests total miscibility PEO-epoxy. In that case, the crystallization should occur through the crosslink structure of the epoxy and it might be expected that a more homogeneous or smoother morphology at room temperature the higher miscibility between the polymers as is observed (Fig. 3). From this explanation, our results suggest (Fig. 3) that from 70 to 140 °C for the curing temperature there is an increase in the miscibility between PEO and the epoxy which is in accordance with the values of W′(PEO) obtained using Eq. (9) and the data of the Table 3.

On the other hand, the epifluorescence images (Fig. 3, right hand side) are blue due to the color of the dansyl group emission, while the morphologies can be observed because of differences in the brightness. Taking into account that most of the scattered light from the sample has been eliminated with a cut filter at 420 nm, the observed blue light must have mainly its origin in the dansyl group fluorescence emission. Therefore, it is reasonable to think that the more emission (intensity) the more brightness.

There are several factors that may affect the fluorescence intensity of the dansyl moiety, mainly: i) the concentration of the chromophore, ii) the nature of the environment (polarity, rigidity) and iii) quenching. Considering that the dansyl groups are chemically attached to a crosslinked epoxy structure, rearrangements of them by diffusion to increase locally its concentration are highly improbable. On the other hand, the PEO has been proven not to be a quencher of the dansyl fluorescence. Therefore, only different environments seem to be the cause of brightness heterogeneity. The polarity effect may be discarded because the difference of polarity between the PEO and the epoxy must be small attending to their chemical structures. However, when the rigidity of the medium increases the fluorescence intensity is enhanced because the number of non-radiative processes is reduced [35]. Therefore, an increase of the emission intensity in the crystalline regions suggests that the rigidity of the medium where the dansyl moiety is located (epoxy) is higher.

The images were obtained at room temperature, below the melting point of PEO. Therefore, it may be considered that the crystallization of PEO causes stiffening of the amorphous phase by reinforcement of PEO spherulites. Similar phenomena were also seen for other compatible amorphous/crystalline polymer blend systems [36, 37].

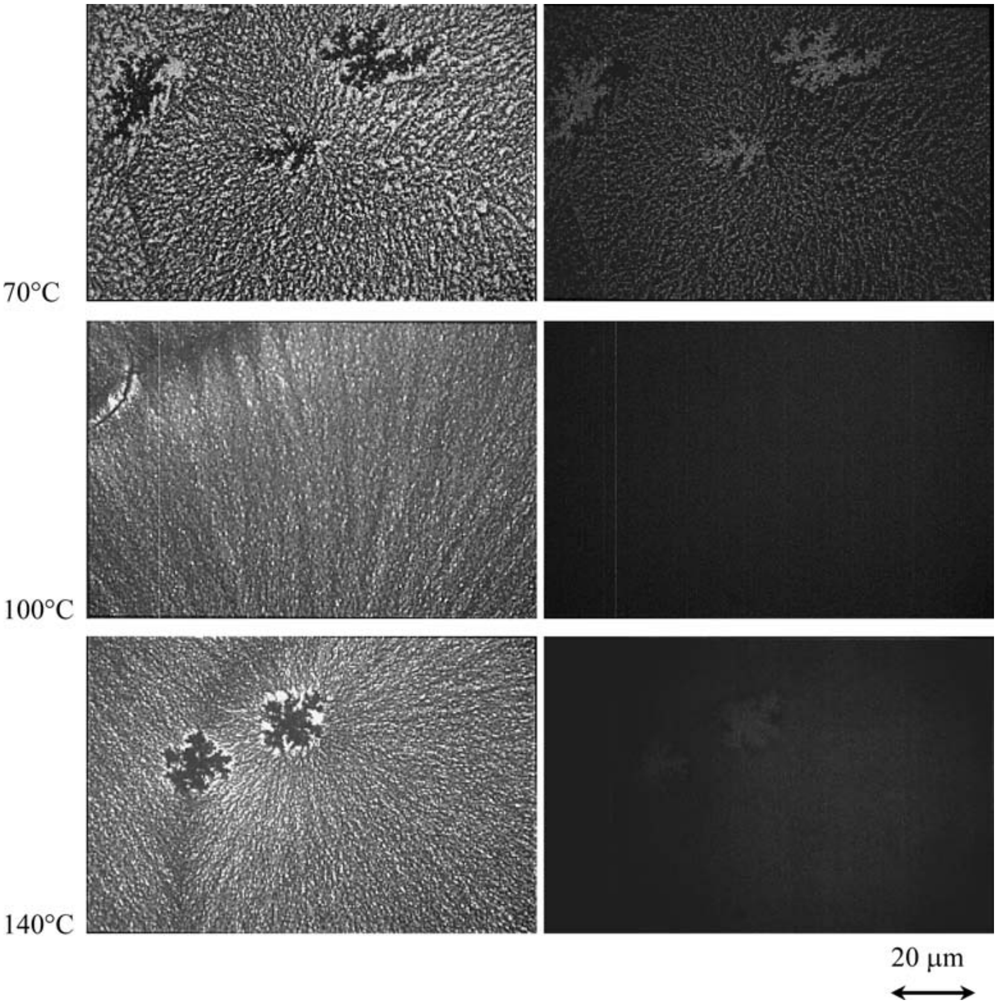

Fig. 3 Optical transmission (*left*) and epifluorescence (*right*) images corresponding to the morphologies of the PEO/epoxy (PEO 30 wt%) cured at different temperatures: 70, 100 and 140 °C respectively

Besides, the fluorescence emission (blue color) is more homogeneously distributed on the images for higher temperatures of curing, which again suggests a higher miscibility between the polymers of the mixture.

In Fig. 4 and Fig. 3 (middle) are presented the morphologies obtained (transmission left and epifluorescence right) as a function of the PEO/epoxy composition for samples that were cured at 100 °C. As can be seen, the kind of crystals formed depends on the composition. When the fraction of PEO is small—10% (Fig. 4, top), the crystals are so small that they cannot be resolved with the lens used for the inspection. When the fraction of PEO is 20% (Fig. 4, bottom) the crystals show a kind of dendritic structure. Although, the dendritic structure observed is quite abnormal, this tree-branch-like PEO spherulites have been reported by Y.P. Huang et al. [13] for an uncured PEO/DGEBA/4,4′-diamino diphenylsulfone epoxy system (PEO/epoxy/DDS). They interpret this morphology in terms of the extent of entrapment of epoxy/DDS molecules within the PEO lamellar bundles. Therefore, if the crystallization rate is high enough to facilitate the entrapment, the same interpretation might explain the dendritic morphologies observed in Fig. 4.

Finally, when the fraction of PEO is 30% (Fig. 3, middle) the crystals show the typical spherulitic structure with a kind of dendritic nucleus similar to those observed when the curing was carried out at 70 °C and 140 °C, top and bottom images respectively in Fig. 3.

The fluorescence image for the sample with 20% of PEO suggests that the crystallization seems to proceed through the epoxy network taking favored paths. Only through specific channels in the epoxy net does the PEO seem to crystallize if it is considered that fluorescence intensity is enhanced in those sites where crystallites stiffens the structure. Another possible explanation may be via the model proposed by Q. Guo et al. [38] for the blend of PEO and DGEBA epoxy resin using 4,4′-methylene-bis(3-chloro-2,6-diethylaniline) as the curing agent. They proposed that the semicrystalline morphology is a stack of crystalline lamellae; the amorphous

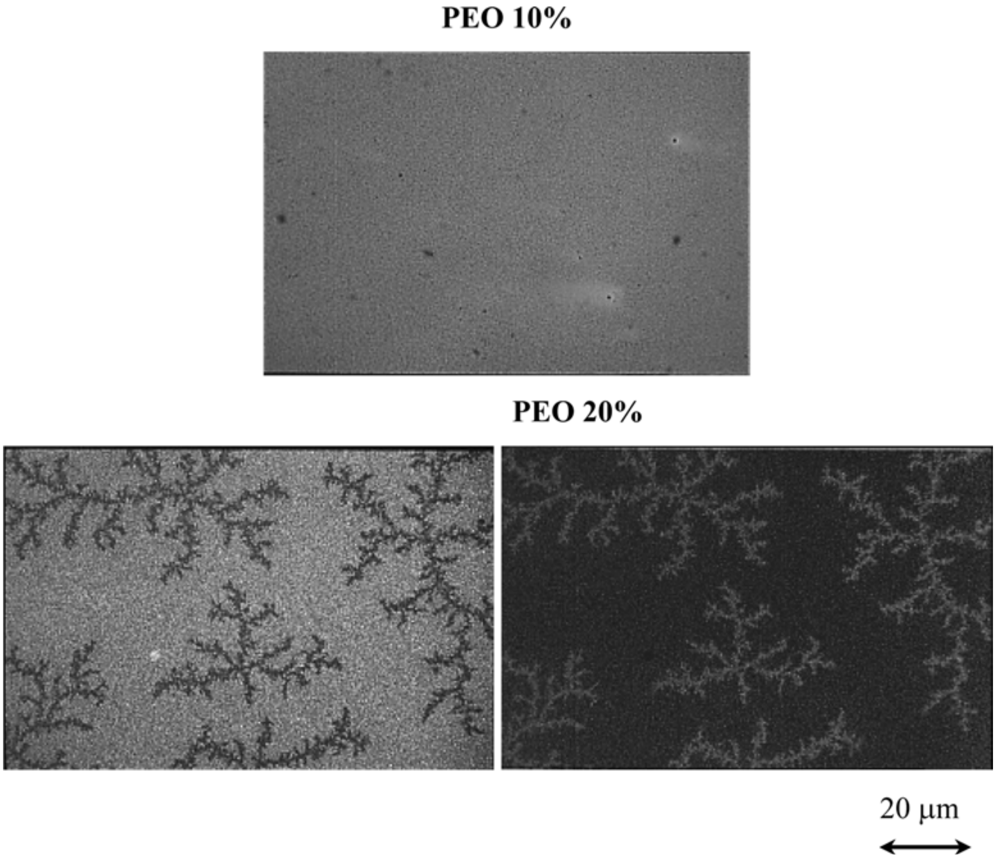

Fig. 4 Morphologies obtained (transmission *left* and epifluorescence *right*) as a function of the PEO/epoxy composition for samples that were cured at 100 °C

fraction of PEO, the branched epoxy resin chains and imperfect epoxy resin network are located between PEO lamellae. If the epoxy resin labeled with dansyl is located between PEO lamellae it would be expected to be a site with more restricted motions. That situation should induce higher fluorescence intensity in those sites which is in accordance with that observed in the fluorescence images.

Finally, Fig. 5 shows the fluorescence spectra for the system PEO/epoxy (PEO 30%) cured at 70, 80, 90, 100, 120 and 140 °C respectively. In all cases a broad band similar to the characteristic one of the dansyl chromophore is observed. However, this band clearly changes as a function of the temperature used to cured the epoxy-amine reactive system, being broader and more shifted to the blue the higher the cure temperature used. This result seems to indicate that there must be a stronger interaction between the dansyl moiety and the PEO the higher the curing temperature, since in every sample the mixture was exactly the same.

It is well known that the fluorescence from dansyl moiety changes depending on its immediate surroundings [21, 22, 23]. An increase in the fluorescence half band width is usually attributed to a wider distribution of sites for a specific fluorophore, as those so-called solvatochromic fluorescence probes or labels (dansyl for example) [35]. Besides, a blue shift for the fluorescence of dansyl immersed in a polymer matrix in the glassy state might be caused by a decrease in polarity at a molecular level near the fluorophore [35].

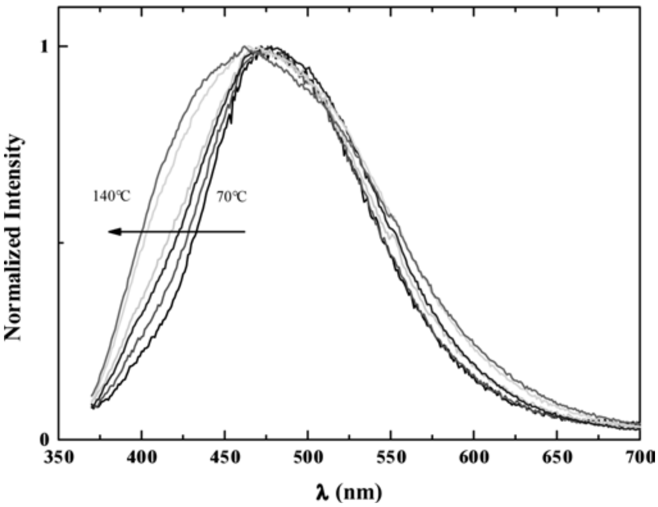

Fig. 5 Fluorescence spectra for the system PEO/epoxy (PEO 30%) cured at 70, 80, 90, 100, 120 and 140 °C respectively

At higher temperatures, if the PEO is getting more miscible in the epoxy matrix (where the dansyl fluorophore is chemically attached), it is reasonable to think that the dansyl fluorescence is more affected. The heterogeneity of the sites where the dansyl is located should increase and the polarity should decrease if it is assumed that the hydroxyls from the epoxy are interacting with the ether groups of the PEO to cause certain miscibility.

On the other hand, it is possible to think that a network difference can also cause a shifting or broadening of the fluorescence band if it is considered that as the epoxy is cured at different temperatures, the network structures and crosslink density should be different. However, under the conditions used in this work (excess of amine functionalities) the above-mentioned should not be very probable, since even at 70 °C there is a complete consumption of epoxy groups (checked by FTIR in the near range).

Therefore, the fluorescence spectra suggest a higher miscibility between PEO and the epoxy network the higher the cure temperature used, in perfect agreement with the results obtained from DSC and morphology.

Conclusions

In this work, the cure kinetic of an ethylenediamine (EDA)-DGEBA mixture modified with PEO was studied. The results obtained suggest that the addition of a non-reactive thermoplastic leads to a dilution effect of the reactive groups and, therefore, to a decrease of the epoxy amine reaction rate. Three methods were used to analyze kinetically dynamic DSC data. One of them is based on a non-catalyzed mechanism, while the others do not consider any specific mechanism but a general one. It seems that the PEO composition does not affect the non-catalyzed process, while an increase in the PEO fraction within the epoxy/PEO yields a decrease of the apparent activation energy that seems to be due to a change in the mechanism of the cure reaction rather than to changes in the catalytic effect. Furthermore, dynamic DSC scans, TOM and EFM images and steady state fluorescence spectra for the cured samples suggest that when the curing temperature increases there is an increase in the miscibility between PEO and the epoxy-amine reaction mixture. On the other hand, the EFM images suggest two possible explanations: i) the crystallization proceed through the epoxy network taking favored paths and ii) the branched epoxy resin chains and imperfect epoxy resin network are located between PEO lamellae. Finally, a reduction of the miscibility between PEO and the epoxy system was observed when the fraction of PEO increases.

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