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Miscibility and mechanical properties of an amine-cured epoxy resin blended with Poly(ethylene oxide)

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Abstract

Blends composed of diamino diphenyl methane-cured bisphenol-A epoxy resin and poly(ethylene oxide) (PEO) were prepared via in situ curing reaction of epoxy in presence of PEO. The miscibility of blends before and after the curing reaction was established by thermal (differential scanning calorimetry, DSC), structural (atomic force microscopy) and dynamic mechanical analysis. Fourier transform infrared spectroscopy indicated that the OH groups developed through cure reactions interact by hydrogenbonding with PEO. After crystallinity analysis by DSC the interaction parameter was determined through the depression of the equilibrium melting temperature. Mechanical properties of miscible blends do not show significant changing however improvement of fracture toughness has been observed respect the matrix properties.

Keywords: miscible blend-mechanical-toughness-melting-crystallinity

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Introduction

Polymer blending is an important alternative to obtain new polymeric materials with designed properties. Thermosets based on crosslinked epoxy resins are used extensively as high performance materials. The main disadvantage of epoxy resins is low impact resistance, which results from their highly crosslinked structures. To improve toughness thermosets polymers are modified by elastomers and thermoplastics to form a phase-separated structure via the process called polymerization-induced phase separation. Although epoxy resins can be substantially toughened by the addition of rubbery phase,¹ the improvement in toughness is inevitably accompanied by a significant loss in modulus and yield stress. Therefore, an alternative approach is to modify epoxy resins with thermoplastic particles with the purpose of achieving enhancement in fracture toughness while retaining other desirable properties. Notwithstanding the mechanical behaviour in a thermoplastic - modified epoxy was improved only if a good adhesion between phases is obtained.² But recently miscible thermosetting polymer blends have been increasing attention for special applications where transparency is desired.

The phase separation process due to the decrease in the configurational entropy of mixing while the molecular weight is increased by the crosslinking reaction can be avoided by strong intermolecular interaction (i.e. hydrogen bonding).³

Several works have demonstrated that the blend of the crystalline poly(ethylene oxide), PEO, with amorphous epoxy resin leads to a miscible material.³⁻¹²

The final properties of a cured epoxy resin blended or not, depend on the cure cycle applied to transform the mixture of epoxy prepolymer and hardener in a crosslinked network.¹³⁻¹⁴ With the aim to study the miscibility and mechanical properties of such a system, we selected stoichiometric mixtures of a diglycidylether of bisphenol-A (DGEBA) cured with 4,4'-diaminodiphenyl methane (DDM), due to our knowledge of

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the cure process,¹⁴⁻¹⁷ modified with PEO due to that published results by Zheng et al⁵ and Larrañaga et al¹⁷ demonstrated the miscibility in this system.

The aim of this work was to characterize the miscibility of these blends by determining the interaction parameter and also to demonstrate the enhancement of thermoset properties of the resulting systems.

Experimental

Materials and sample preparation

The epoxy resin used was DER-332, a DGEBA resin kindly supplied by Dow Chemical, with an epoxy equivalent weight of around 175 g-equiv⁻¹ and a hydroxyl/epoxy ratio close to 0.03. The curing agent was DDM (HT-972), kindly supplied by Ciba, with an amine equivalent weight of 49.5 g-equiv⁻¹. The modifier was PEO with Mw = $8,000 \text{ g-mol}^{-1}$ from Sigma-Aldrich.

Firstly, PEO was added to DGEBA resin at 80 °C and stirred for mixing. Then DDM was added in a stoichiometric amine/epoxy ratio with continuously stirring in an oil bath at 80 °C for approximately 5 min, until a homogeneous blend was achieved.

The cure cycle implies two isothermal steps: the cure step and the postcure step. Two different cure temperatures (Tcure) were selected 80 and 140 °C for 6 and 3 hours respectively, with enough cure time to achieve the gel point in all PEO-modified mixtures. The post-cure step was performed at 190 °C during 2 hours. Samples with low content of PEO were used to study the properties of the modified epoxy (i.e. 0-30 wt%) while samples with high content of PEO were used to determine the interaction parameter through the depression of the melting temperature (i.e. 60-100 wt%).

Characterization and measurements

Glass transition temperatures (T_g) of blends, measured by differential scanning calorimetry (DSC) were taken as the onset point of the step in the heat flow using

dynamical scans from -100 to 50 °C at 20 °C·min⁻¹.

The morphology of tested samples was studied by atomic force microscopy (AFM) with a scanning probe microscope (SPM) (Nanoscope IIIa, Multimode from Digital Instruments) operating in tapping mode under ambient conditions. Etched silicon probes with a cantilever configuration of single beam and 125 mm of length and a tip with a nominal radius of curvature of 5-10 nm were used.

Dynamic mechanical properties were analysed in a Metravib viscoanalyser from 30 to 250 °C at 3 °C·min⁻¹ and 10 Hz using 60x12x5 mm³ samples with a bending device. A constant amplitude of 0.1 V was employed. An initial displacement of 80 μ m was applied to ensure contact between sample and geometry.

Determination of the equilibrium melting temperatures of DGEBA/DDM/PEO system cured at 80 °C and postcured at 190 °C was performed using a Mettler Toledo DSC-822 with nitrogen flux. The isothermal crystallization experiments were carried out using the following procedure: the sample was heated to 100 °C, kept at this temperature for 5 min, rapidly cooled (cooling rate > 40 °C·min⁻¹) to desired crystallization temperature (T_c) and maintained at this temperature for 20 min. After the isothermal crystallization was completed, the sample was cooled to 20 °C and heated to 100 °C at a rate of 10 °C·min⁻¹ for the measurement of the T_m. This procedure was repeated for different crystallization temperatures: 36, 40, 44 and 48 °C.

For the measurement of the crystallinity of PEO in blends with high PEO content fresh samples were heated to 120 °C at 20 °C·min⁻¹, held there for 4 min to eliminate the thermal history; this was followed by cooling to -60 °C at 20 °C·min⁻¹ and a subsequent scan at 20 °C·min⁻¹.

The density of cured samples was measured by weighing three rectangular specimens of each material with well known dimensions.

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The mechanical properties of samples obtained at two curing temperatures (80 and 140 °C) and postcured at 190 °C, with low contents of PEO (i.e. 0-30 wt%) were tested under flexure. Flexural tests were carried out at room temperature (23 ± 2 °C) with a relative humidity of 50 ± 5 % in a Instron universal testing machine Model 4026 with a load cell of 1 kN. Flexural strength and flexural modulus were measured in three-point bending at a crosshead displacement rate of 2.1 mm·min⁻¹ using specimen dimensions of 100×10×5 mm³ with a length between supports equal to 80 mm as recommended by ASTM D-790M-93 standard.¹⁸ Fracture toughness was measured by determining the critical-stress-intensity factor K_{IC}, in three-point bending at a crosshead displacement rate of 1.7 mm·min⁻¹ using notched specimen with dimensions of 60x12x5 mm³ with a length between supports equal to 48 mm as recommended by ASTM D-5045-91 standard.¹⁹ Initially a sharp notch was made by machining and subsequently a natural crack was initiated by using a razor blade. Crack lengths were in accord with the ASTM protocol.

Results and discussion

DSC measurements were carried in order to investigate the initial miscibility of PEO polymer with DGEBA/DDM system. From DSC thermograms the unreacted DGEBA/DDM system presents a T_g of 257 K while the blend modified with 20 wt% PEO shows a single T_g around 245 K. From PPP Handbook ²⁰ the T_g of PEO is 204 K. Thus, PEO was also initially miscible with epoxy system.²¹ Similar results were obtained for samples containing 10 and 30 wt% PEO. The glass transition of a miscible blend can be predicted by using the Fox equation.²²

$$\frac{1}{T_{gblend}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$
(1)

where w_i and T_{gi} are the weight fraction and the glass transition of component i, respectively. Using this equation the predicted T_{gblend} is 244.3 K which is fairly close to the experimentally determined value.

Samples modified with PEO remain transparent after cure thus suggesting the possibility of miscibility in these systems. The morphology of PEO modified systems determined by TM-AFM images at different cure temperatures and PEO contents are shown in Figure 1a-c. At all cure temperatures and modifier contents no phase separation has been observed as height and phase images are quite uniform across the scanned area.

These blends have also been examined using dynamic mechanical analysis to get more information about their state of miscibility. Figure 2 shows storage modulus (E') and tan δ variation with temperature for different PEO contents of samples cured at 140 °C and postcured at 190 °C. A single sharp tan δ peak, corresponding to the α relaxation, that moved to lower temperatures as PEO content increased suggests that the system is miscible.⁵ Similar results were obtained for samples cured at 80 °C and postcured at 190 °C.¹⁷ In Table 1 the corresponding temperature values, T_{gblend}, taken as the maximum in tan δ are shown. This criteria was used because is the same used in a technical application sheet by Triton company ²³ to determine T_g values of PEO (251.1-238.8 K) with low molecular weight (4,000-20,000 g·mol⁻¹). Equation (1) implies that if samples are miscible a plot of 1/T_{gblend} versus the mass fraction of PEO, w₂, must be linear. Figure 3 shows such a plot with a regression coefficient of 0.999 meaning that T_{gl} is 467.3 K, in concordance with experimental value, and T_{g2} is 235.9 K, in the order of reported results.²³

The miscible behaviour of these blends was explained in the bibliography^{3-4,7-8,10-}^{11,24-27} due to the specific intermolecular interaction between the two components. In a

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previous work,¹⁷ we have analyzed FTIR spectra for all cured samples at 80 °C and postcured at 190 °C with different contents of PEO. The broad band centred at 3527 cm⁻¹ was attributed to associated hydroxyl groups while the band centred around 3559 cm⁻¹ was assigned to free hydroxyl groups. The associated hydroxyl group bands shift to lower frequencies as PEO content increases. Moreover, the intensity ratio between associated and free hydroxyl bands increase as the PEO content does. This fact suggests that the OH groups developed through cure reactions interact by hydrogen-bonding with the ether oxygen of PEO. The reason of why epoxy resins cured with aromatic diamines give miscible blends with PEO whereas those cured with aliphatic diamines don't, was explained by Bellenguer et al²⁸ through the study of IR spectra for different epoxidiamine sytems: the higher nucleophility character of the aliphatic nitrogen favours the OH-N interaction leaving less OH free to interact in other hydrogen-bonding.

On the other hand, the Flory-Huggins interaction parameter, χ , quantitatively represents the degree of miscibility of polymer blends. The interaction parameter of amorphous/crystalline blends is usually determined by the equilibrium melting point depression.²⁶ But can be used this method when the amorphous polymer is a highly crosslinked network? We known only one example applied to a miscible PEO/crosslinked polyester blend²⁹ but by using melting temperatures instead of equilibrium melting temperatures; that situation can potentially result in an underestimation of χ .³⁰ So firstly we investigated in bibliography the crystallization of miscible blends of PEO with amine cured epoxy. For high molecular weight PEO blends with DDM cured epoxy, Zheng et al⁵ demonstrated that the system was miscible in all proportions. Woo et al¹⁰ studied miscible blends of PEO with and epoxy cured with diaminodiphenyl sulfone, DDS. By analysing T_g of blends with high content of PEO¹², they suggested that if one disregards the crystalline domains the linear PEO

chains distribute evenly throughout the crosslinked epoxy networks and the morphology of PEO in the cured epoxy/PEO system is quite similar to that observed in the neat PEO. By doing FTIR spectra of PEO extracted with solvent of such samples,¹⁰ it has been demonstrated that the PEO chains interpenetrate by entanglement into the crosslinked epoxy network. Thermodynamically, the PEO chains also intimately mingle with the epoxy-DDS network chain segments to achieve a homogeneous solid state. Guo et al,¹¹ by crystallization studies of miscible PEO blends of 4,4′-methylenebis (3-chloro-2,6-diethylaniline), (MCDEA) cured epoxy resins, conclude that the crystalline morphology of PEO in blends with cured epoxy resin displays typical characteristics of miscible crystalline blends.

Secondly the crystalline behaviour of blends with high content of PEO was evaluated. Figure 4 shows corresponding partial DSC scans. In Figure 4a it is shown that during the heating first scan, the melting peak of fresh samples diminished as PEO content did. While peaks for samples with 60 and 70 wt% PEO have a shoulder at the low temperature region, the peak for the sample with 80 wt% PEO presents a small asymmetry in the left side. A similar effect has been attributed to the presence of two melting temperatures due to crystallization defects in blends of a crosslinked polyester resin and poly(ε -caprolactone)³¹ and it has been also noted in the DSC scan of a sample of a blend of epoxy/DDM with 60 wt% PEO.⁵ Moreover, peaks may also be due to two different types of spherulitic superstructures can be formed, as was reported for blends of syndiotactic polystyrene and poly(styrene-co- α -methyl styrene)³². However, the shoulder of the left side of melting peak is not noticed in a subsequent DSC scan (Fig 4c) after samples were annealed 4 min at 120 °C and cooled at -20 °C·min⁻¹ (Figure 4b). So that, these peaks for fresh samples probably are detected as a result of melting incompletely crystallized spherulites.

The crystallinity of PEO in the blends was calculated with the next equation:

$$X_c = \frac{\Delta H_m}{w \Delta H_m^{0}} 100 \tag{2}$$

where X_c is the crystalline percentage, w the weight fraction of the crystalline component, ΔH_f is the heat of fusion of the blend $\Delta H_m^{0} = 205 \text{ J} \cdot \text{g}^{-1}$ is the heat of fusion of 100 wt% crystalline PEO. ³³ Results are shown in Figure 5. The X_c values for the first heating scan fresh samples are all higher than those for the second heating scans after cooling scan. The crystallization is much more complete in the first scan of fresh samples because of residence time at room temperature.¹¹

Figure 6 shows melting temperatures of the fresh samples first heating scan and that of second heating scan after cooling at -20 °C·min⁻¹. Melting points decrease while decreasing the PEO fraction in the samples. The melting point depression is a common phenomenon for miscible blends containing one crystallizable component. There is not great difference in the depression of melting points between one to other scan. The crystallization temperature during cooling, T_c , decreases while increasing the cured-epoxy fraction, as was also observed by Guo et al.¹¹

The above analysis of the crystallinity allows us to conclude that DGEBA/DDM/PEO blends have a similar behaviour to that shown by other PEO blends with non-crosslinked amorphous polymers. So that, the interaction parameter has been determined through the equilibrium melting point depression. The extensively employed Hoffman-Weeks plot^{11, 32, 34-38} has been used to obtain equilibrium melting temperatures by plotting melting temperatures, $T_{m,i}$, obtained from isothermal crystallizations, versus crystallization temperatures, $T_{c,i}$. The equilibrium melting point of the system, $T_{m,i}^{0}$, was calculated by means of the extrapolation of the experimental curves to the curve $T_{m,i} = T_{c,i}$. Figure 7 shows the corresponding plot. The experimental data can be fitted by the

Hoffman-Weeks equation:³⁴⁻³⁹

$$T_{m,i} = \Phi T_{c,i} + (1 - \Phi) T_{m,i}^{0}$$
(3)

where Φ is the stability parameter which depends on the crystal thickness. The Φ parameter assume values between 0 and 1, $\Phi = 0$ implies that $T_{m,i} = T_{m,i}^{0}$, whereas $\Phi = 1$ implies $T_{m,i} = T_{c,i}$. Consequently, the crystals are more stable for $\Phi = 0.^{26}$ Values of $T_{m,i}^{0}$ and Φ are tabulated in Table 2. The values for Φ parameter are between 0.014 and 0.054 for samples with PEO content between 70 and 100 wt%. This fact suggests that crystals are quite stable.

The data of equilibrium melting points were analyzed with the Nishi-Wang equation⁴⁰ which is based on the Flory-Huggins theory by not taking into account the entropic contribution:

$$\frac{1}{T_m^{0,b}} - \frac{1}{T_m^0} = -\frac{R V_2}{\Delta H_2 V_1} \chi \phi_1^2$$
(4)

where the subscripts 1 and 2 refer to the amorphous and crystalline components, respectively. ϕ is the volume fraction, V the molar volume of the repeating unit, ΔH_2 refers to the fusion enthalpy per mole of 100 wt% crystalline PEO, i.e. ΔH_m^{0} , $T_m^{0,b}$ and T_m^{0} , the equilibrium melting points of blends and that of crystalline component respectively, R, the universal gas constant and χ the interaction parameter. In Figure 8, it is shown the plot of the left term of equation 4 versus ϕ_1^2 and the linearity of the experimental data is quite good. The positive intercept can be related to residual entropic effect. By calculating V₁ as 197.71 cm³·mol⁻¹ and taking V₂ as 38.9 cm³·mol⁻¹, ²⁰ the interaction parameter is -1.077. This negative value explains the miscibility of these DGEBA/DDM/PEO blends in the melt state.³

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As shown in Figure 9, whilst the 30 wt% PEO-modified epoxy system has a flexural modulus clearly lower than that for neat matrix, as a consequence of its lower α relaxation temperature range (see figure 2), the mixtures containing 10 and 20 wt% PEO present a modulus similar or even higher than that corresponding to the epoxy matrix. This fact is possibly related to hydrogen bonding interactions that are responsible for the miscibility and also can modify the free volume of these systems.

As shown in Figure 10, the flexural strength, σ , behaviour of blends is quite similar to that of flexural modulus.

The density, ρ , of the matrix and its blends with 10 wt% of PEO was measured for both cure temperatures to confirm the influence of free volume. Figure 11 shows the relation between E and ρ . The higher modulus values are a direct consequence of the higher density and hence lower specific volume of these networks.

The toughening effect is increased as PEO content and cure temperature increase, as it is shown in Figure 12. The mechanical behaviour of the blends of DGEBA/DDM blends with PEO is similar to those reported by Huang et al⁶ for miscible blends of the same cured epoxy with Bisphenol A-based polysulfone.

Table 3 shows mechanical properties and fracture toughness of DGEBA/DDM/PEO blends for all PEO content and cure temperature for comparison purposes. It is clear that properties of the highly crosslinked epoxies are remain or improve by adding 10 or 20 wt% PEO. The behaviour of the sample modified with 10 wt% PEO cured at 140 °C is specially emphasized as its K_{IC} was increased more than 40 %. On the other hand, the lower K_{IC} for the 10 wt% PEO-modified system cured at 80 °C could be due to small free volume variations that led to a slight increase of stiffness and density.

Conclusions

The miscibility of DDM-DGEBA/PEO blends, due to hydrogen-bonding interactions, was probed in the whole range of compositions. Through the crystallinity analysis it was demonstrated that the behaviour of blends of a crystalline polymer with a thermosetting polymer is quite similar to that of the blends with an amorphous non-crosslinked polymer. Therefore the interaction parameter was determined by the equilibrium melting point depression.

The hydrogen-bonding interactions allow to improve the mechanical properties and fracture toughness with respect to the thermosetting epoxy matrix. The final transparent material has an improvement in toughness without diminish the mechanical properties. This fact does not happen in modified-thermosets polymers obtained via the polymerization-induced phase separation process.

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Figure 1. Height and phase TM-AFM images of epoxy blends modified with PEO homopolymer: a) 10 wt% and cured at 80 °C, b) 20 wt% and cured at 80 °C and c) 20 wt% and cured at 140 °C. All samples were postcured at 190 °C for 2h.



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Figure 2. Storage modulus (E') and loss factor (tan δ) variation upon temperature for pure DGEBA/DDM and its blends modified with different contents of PEO, cured at 140 °C and postcured at 190 °C.







Figure 4. DSC scans for high PEO contents in blends of cured epoxy/PEO.a) Fresh sample first heating scan, b) cooling scan at -20 $^{\circ}C \cdot min^{-1}$ and c) second heating scan after cooling at 20 $^{\circ}C \cdot min^{-1}$.

Figure 4a. DSC scan of fresh samples





Figure 6. Melting temperatures measured in fresh sample heating and second heating DSC scans, and crystallization temperature in cooling DSC scan versus composition of blends.

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Figure 10. Flexural strength of epoxy blends as a function of the weight fraction of PEO in blends for different cure temperatures.

Figure 12. Critical-stress-intensity factor as a function of the weight fraction of PEO in blends for different cure temperatures.

PEO (wt%)	T _{gblend} (K)						
	Tcure = 80 °C	Tcure = 140 °C					
0	466.5	468.2					
10	427.7	426.8					
20	391.4	392.2					
30	363.5	358.9					

Table 1. Glass transition temperatures determined as the maximum in tan δ peak

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Table 2. Values of equilibrium melting point and stability parameter for epoxy/PEO blends.

PEO (wt%)	$T_{m,i}^{0}(\circ C)$	Φ
10	65.0	0.054
90	62.6	0.031
80	61.7	0.022
70	60.6	0.014

PEO
(wt%) $T_{m,i}^{0} (°C)$ Φ 1065.00.0549062.60.0318061.70.0227060.60.014

PEO	Tcure = 80 °C			Tcure = 140 °C		
(wt%)	E (MPa)	σ (MPa)	$\frac{K_{I,c}}{(MPa m^{1/2})}$	E (MPa)	σ (MPa)	$\frac{K_{I,c}}{(MPa m^{1/2})}$
0	2330 ± 25	94,4 ± 1.01	0.90 ± 0.05	2425 ± 45	94,5 ± 1.79	1.03 ± 0.067
10	2615 ± 20	103,9 ± 1.23	1.06 ± 0.034	2530 ± 45	98,3 ± 1.48	1.47 ± 0.066
20	2540 ± 30	95,2 ± 1.73	1.48 ± 0.063	2500 ± 35	91,6 ± 1.3	1.59 ± 0.064
30	1560 ± 45	53,6 ± 1.14	1.56 ± 0.057	1210 ± 60	42,2 ± 1.84	1.60 ± 0.084

 Table 3. Mechanical properties and fracture toughness of DGEBA/DDM/PEO blends