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Thermal behaviour of unsaturated polyester resins + poly(3-octylthiophene) blends

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Abstract

Blends of poly(3-octylthiophene) (POT) with unsaturated polyester (UP) resin have been investigated. Two glass transition temperatures, T_g, were detected by differential scanning calorimetry (DSC) in blends of POT + uncured polyester resins, which indicate the partial immiscibility of these systems. It has been demonstrated that the miscibility behaviour of these blends depends up to a point on the solvent used in sample preparation. Also POT was found to be immiscible with crosslinked polyester resins which was concluded from the results of thermal analysis. The influence of the presence of POT on the crosslinking reaction, the miscibility of the crosslinked system and finally the melting behaviour of POT were analysed. The results obtained have been compared in the crosslinked and uncrosslinked blends. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Conducting polymers; Polyester resins; Poly(3-octylthiophene); Glass transition temperature; Phase behaviour

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1. Introduction

Conducting polymers have attracted much attention during the last few years because of potential technological applications [1]. The use of conducting polymers in technological applications has been precluded by their poor processability and high cost. Even though there exits a reasonably good level of understanding about the conducting mechanisms in these materials [2], the principal problems encountered with the practical utilisation of these polymers are processability and environmental stability. Blending insulating polymers with conducting polymers is an attractive route to improving mechanical properties without loosing conductivity.

On the other hand, unsaturated polyester (UP) resins are the most widely used thermosets in polymeric composites [3] due to advantages such as high strength, dimension stability, low weight, good corrosion properties and low price [4]. Extensive research has been developed on the curing of UP resins in the literature [5–10]. The crosslinking reaction of UP resins is a free radical chain growth crosslinking copolymerisation between styrene monomer and UP molecule. Polyester molecules are the crosslinkers while styrene serves as an agent to link the adjacent polyester molecules, as a consequence the crosslinked structure of cured polyester resins is complex and inhomogeneous [8].

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Unfortunately most of the blends containing conducting polymers have been found to be immiscible [11–13], although, in recent years binary blends showing a miscibility window have been reported [14–16].The aim of this work is to investigate the possible miscibility between thermosetting polymers as UP resins and a conductive polymer poly-(3-octylthiophene) (POT). The work has been divided in two parts. On the one hand, the miscibility of POT and uncured polyester resin has been studied by thermal analysis. The influence of the solvent used in the sample preparation on the miscibility behaviour of these blends has been detected. Blends of UP resins crosslinked in presence of POT have been also investigated, and in order to simplify the morphology of this blends the UP resins have been crosslinked without styrene. The influence of POT on the curing reaction and the miscibility behaviour observed for the crosslinked and uncrosslinked blends will be discussed. Finally, the melting behaviour of POT in uncrosslinked blends will be compared with that in crosslinked blends.

2. Experimental

2.1. Materials

POT were obtained from Polysciece (Germany). Gel permeation chromamatography (GPC) from tetrahydrofurane solutions gave the following values for number average molecular weight, $M_n = 14{,}700$ and polydispersity index $r = 4$.

The UP resins (Estratil AL-100 and Estratil 6603) were provided by Plastiform (Spain). The resins were dissolved in chloroform and precipitated in methanol in order to remove styrene contained in the commercial resins. Nuclear magnetic resonance (NMR) spectroscopy was used to characterise the resins. The Al-100 resin consisted of phthalic anhydride (PA), maleic anhydride (MA), and 1,2-propylene glycol (PG) and the 6603 resin is a isophthalic resin that contains isophthalic acid (IA) instead PA. The M_n calculated from the acid value, the relative composition of both resins and the double-bond content expressed in mole of insaturations by unit weight of resin are shown in Table 1 for UP resins.

In the crosslinking reactions, the initiator was benzoyl peroxide at 1 wt.% of the total resin mass. This concentration was enough to give a maximum rate of reaction when scanning at a constant heating rate in the DSC.

2.2. Sample preparation

The blends were prepared by casting from solution an appropriate amount of each polymer in three solvents: chloroform (CL), toluene (TOL) and tetrahydrofuran (THF). The solutions were first left until most of the solvent had evaporated at room temperature, and then the solvent was removed in a vacuum oven at 50 °C.

2.3. Differential scanning calorimetry

The glass transition temperatures (T_g), and the melting points were measured using a Mettler model 829 DSC calorimeter at a standard heating rate of 20 K min^{-1}. The temperature scale was calibrated from the melting point of indium. In all of the cases, open aluminium pans were used with sample weights ranging from 5 to 10 mg and the measurements were carried out under dry N_2 atmosphere. The glass transition temperatures were taken as the midpoint of the heat capacity transition. The melting points, T_m, was taken as the maxima of the transition. The values of T_g and T_m were obtained from the second scan.

Table 1
Relative composition obtained from ^{1}H NMR, number average molecular weight, M_n, and double-bond content of 6603 and AL-100 resins

UP resin	Relative composition			Double-bond content (mol g^{-1})	M_n
	PA and IA	MA	PG		
AL-100	2.51	1	3.66	1.52×10^{-3}	2300
6603	1.19	1	2.34	2.61×10^{-3}	3700

Table 2
Glass transition temperatures, T_g, for UP resins (6603 and AL-100)[a]

Resin	Solvent	T_g (°C) (first scan)	T_g (°C) (second scan)	T_{exo} (°C) (first scan)	ΔH_{exo} (J g^{-1})
Al-100	THF	–	38.9	–	–
Al-100	TOL	–	38.4	–	–
Al-100 + benzoyl peroxide (1%)	TOL	21.4	47.1	147.6	−55
6603	THF	–	51.2		
6603	CL	–	51.2	–	–
6603	TOL	–	47.6	–	–
6603 + benzoyl peroxide (1%)	TOL	39.2	57.8	145	−78

[a] Temperature, T_{exo}, and heat of curing reaction ΔH_{exo}, per unit mass of AL-100 and 6603. The solvent used in the preparation of polymer samples are reported in each case.

3. Results and discussion

3.1. Pure polymers

The T_g values of 6603, AL-100 are shown in Table 2 along with the solvent used in the preparation of the samples is mentioned in each case. For samples of 6603, AL-100 and POT prepared in presence of benzoyl peroxide, Table 2 shows the T_g values corresponding to the first and second scans, in all other cases only the T_g value corresponding to the second scan is given. T_g for 6603 is higher than T_g for AL-100 regardless of solvent used. For 6603 and AL-100 samples with benzoyl peroxide, the first scan shows a glass transition and an exothermic peak located at the temperature, T_{exo}, and corresponding to the overall heat of reaction $(\Delta H)_{exo}$ of double bonds of AL-100 and 6603 resins. Table 2 gives the values of T_{exo} and ΔH_{exo} expressed per unit mass of resin. Reported value for the heat evolved in the homopolymerisation of diethyl ester of fumaric acid (taken as a model system of unsaturated resins) is 65 kJ mol^{-1} (per mole of double bonds) [17]. Comparing this value with the values of ΔH_{exo} in Table 2 and taking into account the double-bond content of the resins (Table 1), it is possible to estimate the maximum conversion attained for 6603 and AL-100 in the curing reaction, being 46 and 56% for 6603 and AL-100 resins, respectively. The effect of the crosslinks is observed comparing the T_g values for AL-100 and 6603 obtained from the first and second scans for 6603 and Al-100 resins, i.e. before and after the curing reaction.

The change in the heat capacity corresponding to T_g for POT is only detected with certainty for POT samples prepared by casting from TOL solutions as can be seen in Table 3. If the solvent used was either THF or CL, in the range of temperature corresponding to the glass transition, it is possible to detect a little change in the slope of the heat capacity. The measured curves for POT in TOL cast-samples are showed in Fig. 1 and the T_g obtained was in accordance with the values of T_g reported in the literature [13,16], although there was no significant change in T_g for POT containing benzoyl peroxide in comparison with POT casting from TOL.

Table 3 also contains information about the melting behaviour of POT. The melting endotherm for POT was broad and weak as it is shown in Fig. 1, consequently there was some uncertainty in determining the melting temperature. As can be observed the values of melting temperature, T_m, and melting heat, ΔH_m for POT samples obtained by casting from THF, CL and TOL solutions are similar. The values of T_m in Table 3 are lower than the bibliographical value ($T_m = 160$ °C) [16]; the difference could be explained by taking into account the difference in the molecular

Table 3
Melting temperature, T_m, and melting heat per unit mass of polymer, ΔH_m, for POT[a]

Polymer	Solvent	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})
POT	THF	–	145	5.8
POT	CL	–	147	4.6
POT + benzoyl peroxide (1%)	TOL	−16	137	3.6
POT	TOL	−17.5	149	6

[a] The solvent used in the preparation of polymer samples are reported in each case.

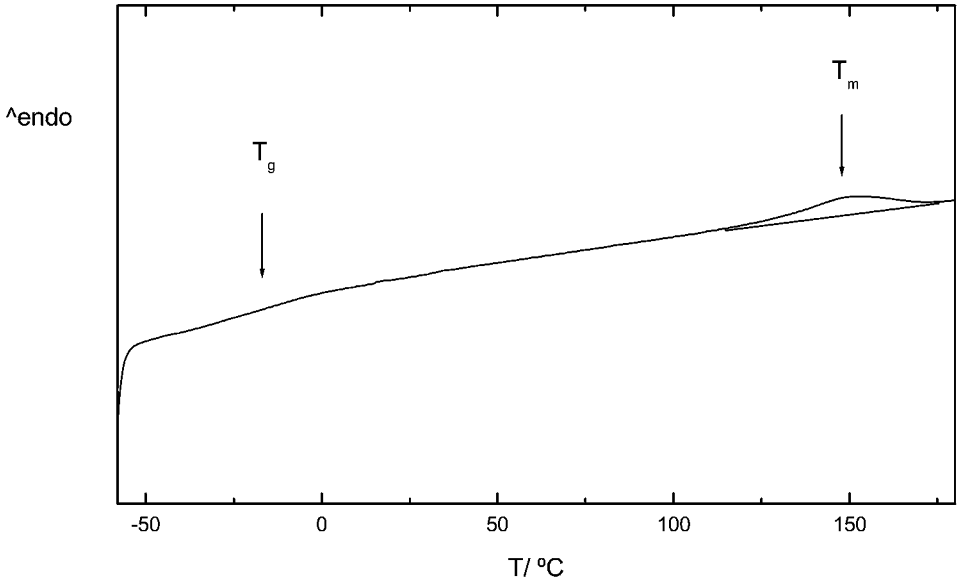

Fig. 1. Thermo-analytical response of POT sample prepared by casting from a solution in TOL.

weights of both samples of POT [16]. For solutions, cast-samples obtained in presence of benzoyl peroxide a decrease in the values of T_m and ΔH_m were observed.

3.2. Blends AL-100 + POT and 6603 + POT casting from THF and TOL

The miscibility behaviour of these blends was be analysed from the dependence of T_g with the blend composition expressed as weight fraction of POT in the blend, W_{POT}. The results obtained from AL-100 + POT and 6603 + POT blends casts from THF and TOL are shown in Figs. 2 and 3, respectively. Fig. 2 exhibits one T_g in both A and B cases, that corresponds to polyester resins over the entire composition range; for $W_{POT} > 0.7$ a second T_g appears that corresponded to that of POT. This behaviour is in accordance with incompatible blends, of separated amorphous phases of POT and 6603 or AL-100 resins.

TOL cast-samples as shown in Fig. 3 also behave typically as incompatible blends. However, there are some differences when they are compared with THF cast-samples. In 6603 + POT two T_g are found over the entire composition range: one T_g has the same value over the whole composition range equal to 6603 T_g value and a second T_g, slightly higher, corresponding to POT. In AL-100 + POT the behaviour is similar although the lower T_g only appears for $W_{POT} \geq 0.4$. In these blends the amorphous phase is separated into two different domains, but while one of them corresponds to AL-100 or 6603 resins the other is POT with a small quantity of resin added. If the Fox equation applies to the miscible phases [18], i.e.

$$\frac{1}{T_g} = \frac{W_{POT}}{T_{g,POT}} + \frac{1 - W_{POT}}{T_{g,resin}} \tag{1}$$

the amount of resin dissolved in the POT phase can be determined for the constant value of T_g corresponding to the composition range $0.2 \leq W_{POT} \leq 0.9$ and $0.4 \leq W_{POT} \leq 0.9$ for 6603 + POT and AL-100 + POT blends, respectively. In Eq. (1) $T_{g,resin}$ and $T_{g,POT}$ refer to the T_g value of 6603 or AL-100 and POT and T_g is the constant value of T_g, that is $T_g = -14$ °C for AL-100+ POT blends and $T_g = -11$ °C for 6603 + POT blends. From Eq. (1) it is estimated that POT has up to 7% (w/w) of AL-100 resin and up to 12% (w/w) of 6603 resin. Therefore, the T_g results for 6603 + POT and AL-100+ POT casting from TOL seems to indicate that the solvent used in the preparation of samples has some influence in the phase-behaviour of the blends.

It is well known that the melting behaviour of crystalline polymers depends on the phase behaviour

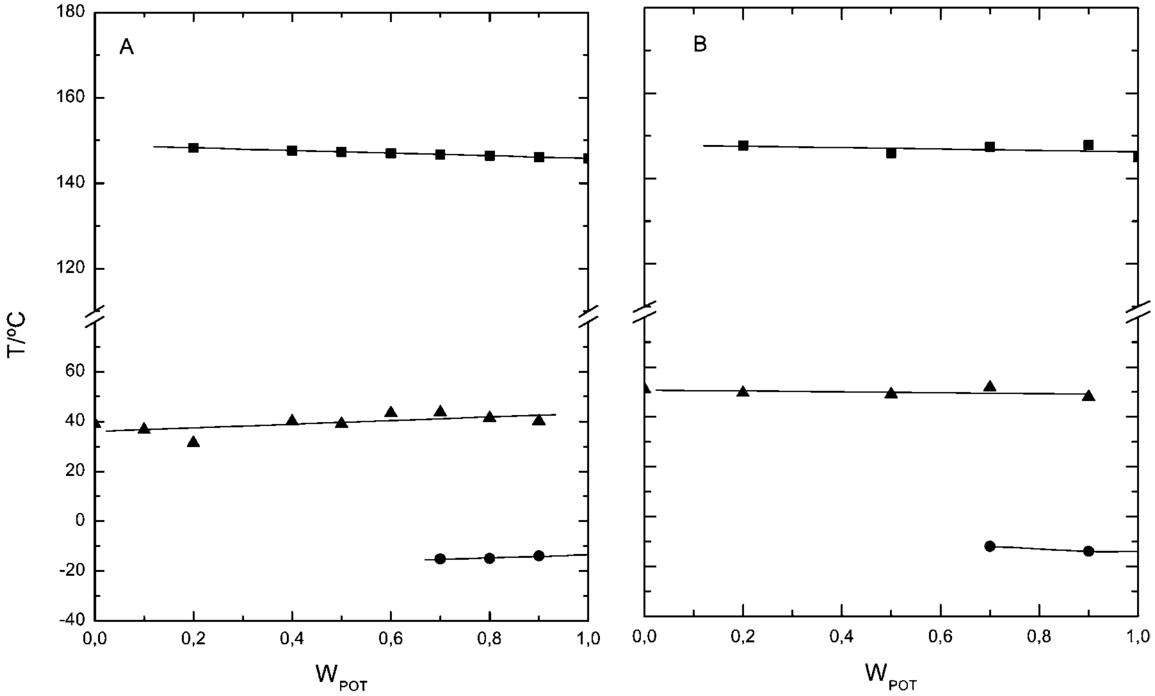

Fig. 2. Dependence of melting temperature (■), and glass transition temperature (▲, ●) on the weight fraction of POT, W_{POT}: (A) Al-100 + POT and (B) 6603 + POT cast from THF.

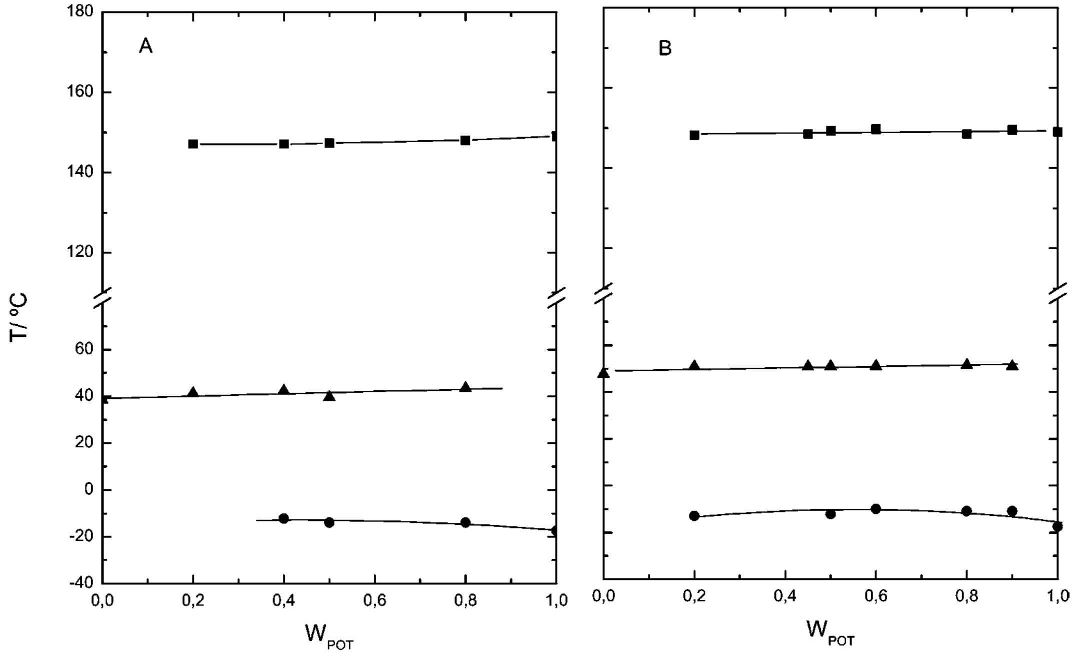

Fig. 3. Dependence of melting temperature (■) and glass transition temperature (▲, ●) on the weight fraction of POT, W_{POT}: (A) AL-100 + POT and (B) 6603 + POT cast from TOL.

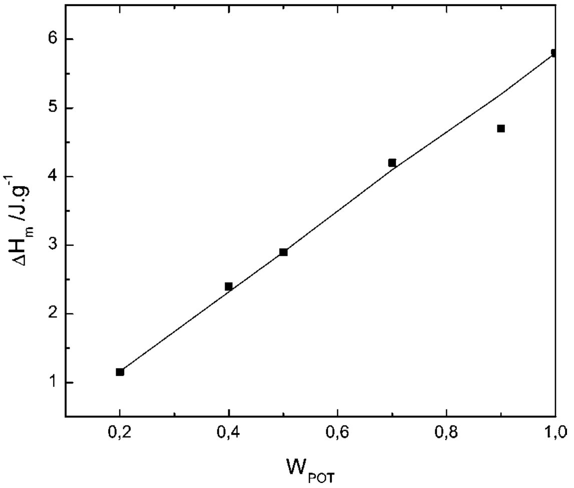

Fig. 4. Heat of fusion per unit mass of blend sample, ΔH_m vs. W_{POT}, for AL-100 + POT blends cast from THF. The line represents the ideal behaviour in which resin does not interfere with POT crystallisation.

of the blends. In miscible blends comprising of a semicrystalline polymer and an amorphous polymer is very common to observe a depression in the melting point, also the ability to crystallise is usually suppressed in some blends compositions [19–21]. The melting behaviour of POT in 6603 + POT and Al-100 + POT blends casting from THF and TOL has also been studied. The measured curve exhibit a broad and weak endotherm corresponding to the melting of POT crystals. The melting temperature T_m and the heats of fusion per unit mass of POT in the sample, ΔH_m, as a function of the blend composition can be estimated from the different endotherms. The results of T_m versus W_{POT} are showed in Figs. 2 and 3. Taking into account that all the blends have the same behaviour, Fig. 4 shows, as an example, ΔH_m versus W_{POT} in AL-100 + POT blends casting from THF. It is apparent that POT crystallises from blends to about the same extent as it does in the pure state. These results are in agreement with phase separation observed in the studied blends.

3.3. AL-100 + POT and 6603 + POT blends: curing systems

The reaction of UP resin (6603 and AL-100) is a free radical chain growth crosslinking copolymerisation between the styrene monomer and UP molecule. Polyester molecules act as crosslinking agent while styrene links the adjacent polyester molecules. In order to simplify the crosslinked structure of UP resins, the crosslinking reaction of UP molecules,

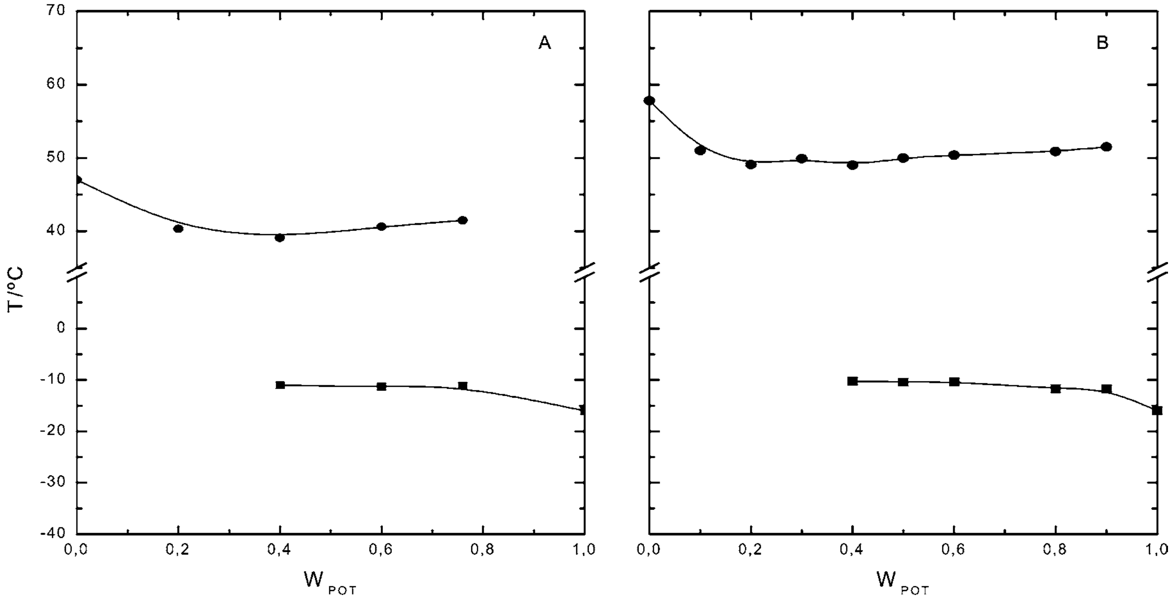

Fig. 5. Dependence of glass transition temperature on the weight fraction of POT, W_{POT}: (A) IPNAL-100 + POT and (B) IPN6603 + POT.

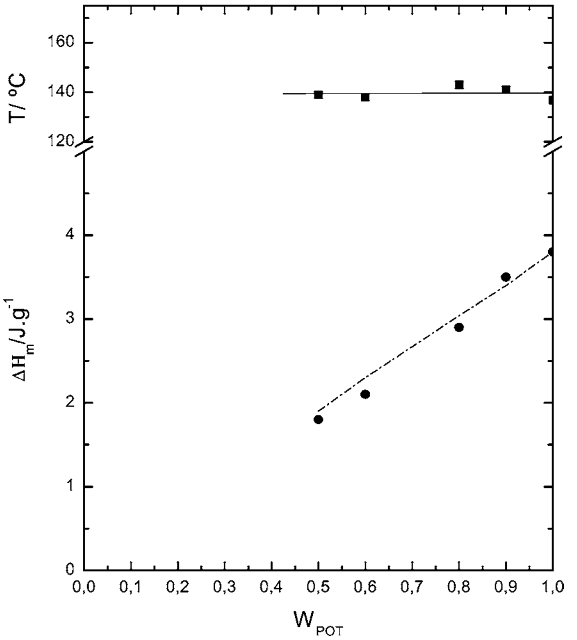

Fig. 6. Dependence of the melting temperature (■) and heat of fusion per unit mass of the sample blend (●), ΔH_m with W_{POT}, for IPN6603 + POT: (-·-·-) represents the ideal behaviour in which the crosslinked resin does not interfere with POT crystallisation.

through C=C bonds, was carried out without styrene, using benzoyl peroxide as initiator in TOL cast-samples of AL-100 + POT and 6603 + POT blends. From a structural point of view these blends could be considered as semi-interpenetrating networks in which a linear polymer coexists with a crosslinked structure of UP resins (AL-100 or 6603). To distinguish these blends from now on, the prefix IPN will be used.

Fig. 5 shows the T_g as a function of W_{POT} for the crosslinked blends: case A is the IPNAL-100 + POT and case B IPN6603 + POT. Two T_g were observed over the whole composition range indicating the immiscibility of the systems. Fig. 6 shows T_m and ΔH_m per unit mass of blend sample, for IPN6603 + POT. These were in agreement with the immiscibility of the system. The same behaviour was observed for IPNAL-100 + POT.

As can be seen from the results on the T_g, T_m, and ΔH_m, the behaviour of IPNAL-100 + POT and IPN6603 + POT was similar to those obtained for the blends without crosslinking. However, there were some differences that should be explained. By comparing Fig. 5 with Figs. 2 and 3, it can be seen that in the crosslinked blends the value of the highest T_g at each W_{POT} was lower that the corresponding one of the pure crosslinking resins 6603 and AL-100, accordingly crosslinked AL-100 and 6603 contained a small amount of POT, also the lower T_g obtained at each W_{POT}, was higher than the T_g value of POT. Therefore, IPNAL-100 + POT and IPN6603 + POT blends separated into two amorphous regions, like uncrosslinked blends, AL-100 + POT and 6603 + POT. However,

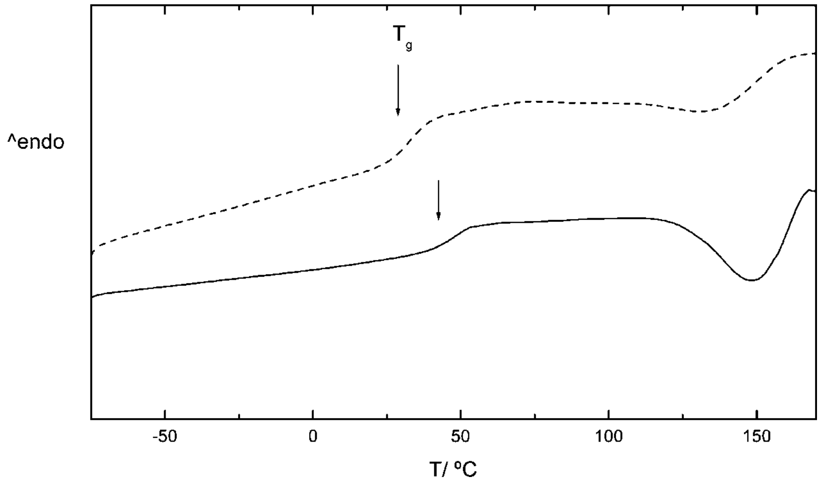

Fig. 7. Thermo-analytical curve corresponding to the first scan: (—) IPN6603; (- - -) IPN6603 + POT (W_{POT} = 0.2). The exothermic peak is attributed to crosslinking reactions through C=C bonds of the resin.

the results suggest that a certain level of miscibility is reached in the crosslinking systems. Nevertheless, from the thermodynamic point of view, an increase in molecular weight for either of the components of blends would decrease the cloud-point temperature, which should be a negative contribution to the miscibility in contrast to the behaviour observed in such blends containing one component highly crosslinked (high molecular weight). This surprising behaviour can be explained by analysing the heat generated in the cure reaction of the AL-100 and 6603 resins in the IPN blends.

The first scan in the measured curve of IPN6603+ POT and IPNAL-100 + POT blends shows a single exothermic peak at 135 °C in the composition range $0 \leq W_{\mathrm{POT}} \leq 0.3$ which is attributed to crosslinking reactions (see Fig. 7). Above $W_{\mathrm{POT}} = 0.3$, the exothermic peak is not detected although it could be masked by the melting peak corresponding to POT.

Since only the Al-100 and 6603 resins are capable of crosslinking, the heat of reaction expecting from IPN blends can be calculated as

$$\Delta H_{\mathrm{exob}} = \Delta H_{\mathrm{exo}} \times (1 - W_{\mathrm{POT}}) \tag{2}$$

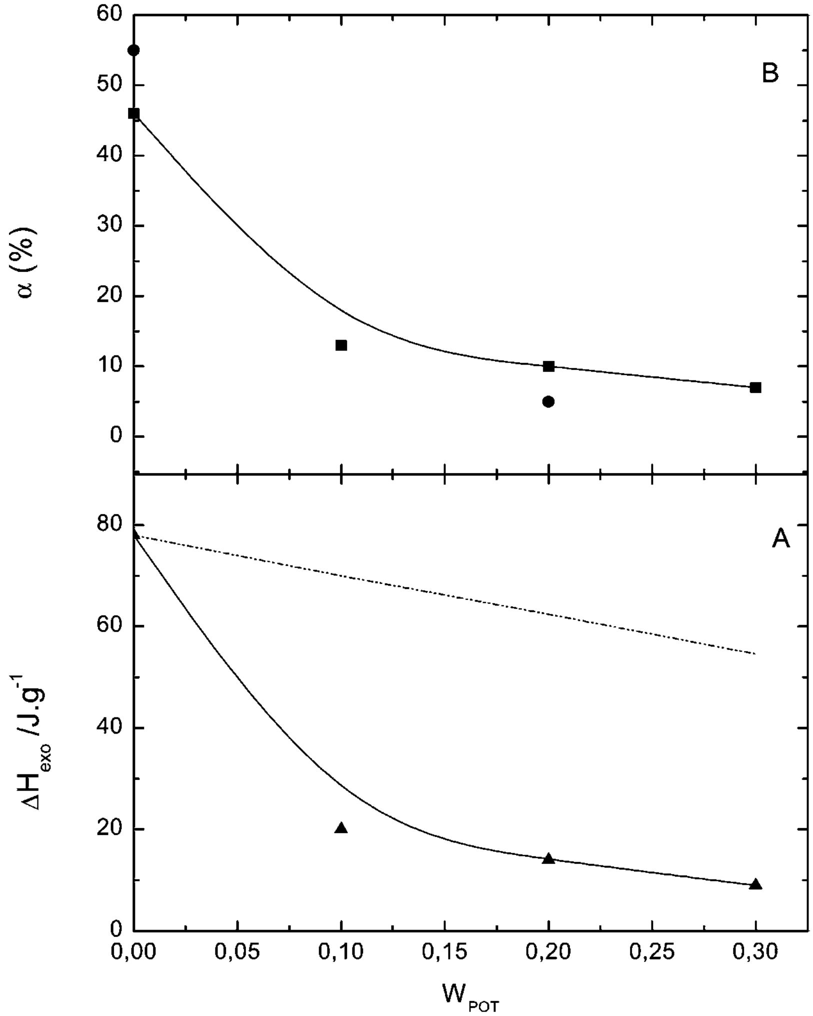

Fig. 8. (A) Heat of reaction, H_{exo}, of IPN6603 + POT blends as a function of weight fraction of POT, W_{POT}, in the blend: (-·-·-) represents the heat of reaction calculated from Eq. (2). (B) Polyester double-bond conversions, α, in IPN blends: (■) IPN6603 + POT blends; (●) IPNAL-100 + POT blends.

where ΔH_{exo} (J g^{-1}) is the heat of reaction of AL-100 or 6603 pure resin and ΔH_{exob} (J g^{-1}) is the expected heat of reaction of AL-100 and 6603 in the IPN blends, both expressed per unit mass of total sample. Fig. 8 shows the experimental results comparing with those obtained from Eq. (2). As it can be observed the results are located below the expected heat calculated from Eq. (2), in the composition range $0 < W_{\text{POT}} \leq 0.3$. Since this equation is derived from a simple rule of mixtures, the negative deviation observed in the experimental heats of reaction means that AL-100 and 6603 in the blends have less capacity for crosslinking than in pure state.

The polyester double-bond conversions, α, in IPN blends as a function of WPOT can be calculated as

$$\alpha = \frac{\Delta H_{\text{exp}}}{\Delta H_{\text{mod}}} \times 100 \tag{3}$$

where ΔH_{exp} is the experimental heat of reaction expressed per mole of insaturations at each composition and $\Delta H_{\text{mod}} = 65$ kJ mol^{-1} corresponds to the homopolymerisation of diethyl ester of fumaric acid taking as a model system of UP resins [17]. The data of versus W_{POT} are plotted in Fig. 8. α falls suddenly for low contents of POT in the blends, changing from $\alpha \approx 50\%$ for pure resins AL-100 or 6603 to 10% for $W_{\text{POT}} = 10\%$. Data shown in Fig. 8 confirm that the crosslinking reaction between polyester chains is hindered by the presence of little amounts of POT and for $W_{\text{POT}} > 0.3$ is not detected. A possible explanation for this behaviour is that the of benzoyl peroxide is distributed in a different way between the two phases in the IPN blends, interacting preferentially with the rich POT phase. This would result in a fall in the amount of initiator in contact with phase rich in resin and a decrease in the extent of the crosslinking reaction. Therefore, the decreasing in the T_g values of crosslinked AL-100 and 6603 resins observed in Fig. 5 for IPN blends is a consequence of the decreasing in the crosslinking density and so it could not be attributed to the existence of a certain degree of miscibility in the IPN blends. Therefore, the amorphous phase in IPN blends seems to be constituted by two different domains, AL-100 or 6603 pure resins lightly crosslinked and POT that accepts small quantity of resin. This quantity can be determined from the constant value of T_g, corresponding to these domains $T_g = -11$ °C for IPNAL-100 + POT and $T_g = -10$ °C for 6603+ POT. Using the Eq. (1) it follows that in IPN blends, AL-100 + POT and 6603 + POT, the region enriched in POT admit in both cases approximately the same quantity of pure resins that uncrosslinked blends.

4. Conclusions

Blends of POT and UP polyester resins (6603 and AL-100) have been investigated by DSC. In the uncrosslinked blends: 6603 + POT and AL-100+ POT the results of T_g as a function of the blends composition reveal the existence of two different regions in the amorphous phase confirming the immiscibility of these systems.

The crosslinked blends: IPN6603 + POT and IPNAL-100 + POT are produced by crosslinking polyester resins in the presence of linear chain of POT. The T_g measurements as a function of the blends composition are in accordance with the behaviour corresponding to immiscible blends. In the other hand, it has been demonstrated that the presence of POT influences the curing reaction with a decrease in the crosslinking density of the polyester resins.

The thermo-analytical responses show broad melting endotherms corresponding to POT. The melting temperature and heat of fusion of crystalline POT are not dependent on the concentration of polyester resins in crosslinked and uncrosslinked blends. Consequently, the crystallisation of POT is not disturb by the presence of AL-100 or 6603 resins. This behaviour is in agreement with the phase separation detected in the blends studied.

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