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EPOXY/POLY(4-VINYLPHENOL) BLENDS CROSSLINKED BY IMIDAZOLE INITIATION

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Poly(4-vinylphenol) (PVPh) was used as thermoplastic modifier of epoxy resins. Binary epoxy/PVPh mixtures with high thermoplastic content rise high glass transition temperatures (T_g) after heating, due to the epoxy-phenol reaction. Blends with low PVPh percentages reach high T_g if 2-methylimidazole is added, which catalyses epoxy homopolymerisation and epoxy-phenol reaction. The cured blends do not present phase separation although the network structure depends on the epoxy/phenol ratio. At low PVPh percentage the main crosslinking reaction is epoxy-epoxy but, when the thermoplastic content increases, the epoxy-phenol reaction prevails, causing an important T_g increase and becoming less brittle.

Keywords: *curing, epoxy blend, imidazole, poly(4-vinylphenol)*

Introduction

Thermosetting epoxy resins are widely used as structural adhesives, coatings and matrix of fiber-reinforced composites. They usually present high tensile and compression strength, good adhesion properties and high thermal and chemical resistance. Their final properties depend on the nature of epoxy pre-polymer and curing agent, on the composition and overall on the curing conditions [1, 2]. Epoxy crosslinking process can be carried out through two different polymerization reactions. The most common curing process is based on the use of hardeners, such as amines, anhydrides, phenol novolacs and isocyanates. In this case, the crosslinking occurs through a step-growth reaction [1, 2]. On the other hand, the epoxy network can be also yield by chain-growth homopolymerisation using tertiary amines as initiators [3–6]. In both curing processes, imidazoles have been used as initiators and catalysers. They can be added to epoxy-anhydride systems as estherification initiators [7], and to epoxy-phenol system, as selective catalysers of epoxy-phenol reaction [8–10]. Also imidazoles act as initiators of epoxy homopolymerization process [3–6].

The epoxy/phenol resins and the homopolymerised epoxy resins are widely used in the electronics industry as encapsulating, packing and sealing materials. Nevertheless, there is still a lack of knowledge about them, associated to the high complexity of involved reaction mechanisms. For instance, little is known about the selectivity and efficiency of imidazoles when different reactions can compete in an epoxy/phenol system, due to the high number of parameters which affect to the curing process. Several researchers [3–10] have demonstrated that the final properties of these resins depend on numerous factors, such as the epoxy/phenol ratio [8–10], the nature and position of substituent groups of imidazole [4, 5], the catalyser concentration [4, 5, 9] and the curing temperature [3, 8].

In the last years, most studies about epoxy resins are related to the toughness modification by the addition of thermoplastic or rubber polymers [11–13]. Thermosetting/thermoplastic blends are materials resulting from the mixing of a thermoplastic polymer and epoxy precursors (epoxy pre-polymer and curing agent), and the subsequent reaction of the precursors. Usually the initial mixture is homogeneous, but as the epoxy molar mass increases, liquid-liquid phase separation occurs. Thus the obtained cured blends generally present phase separated morphology. However, in a recent study, Woo *et al.* [14] found a homogenous epoxy/thermoplastic blend, which was formed by an epoxy resin cured with amine hardener and modified with poly (4-vinylphenol) (PVPh). They also observed that the heating of binary mixture of DGEBA with high PVPh content provided a homogenous material presenting high T_g [15]. They justify this behaviour by the reaction between the epoxide rings of epoxy monomer and the phenol groups of PVPh, which spontaneously occurs above 180°C.

In this work, an imidazole has been added to the initial epoxy/PVPh mixture, as initiator/catalyser agent. In principle, the imidazole can act as catalyser

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of both, epoxy homopolymerisation and epoxy-phenol reaction. Therefore, the main objective was to yield homogenous epoxy/PVPh blend with low thermoplastic content and to determine its main characteristics. The curing process and the final network structure have been studied as a function of the thermoplastic content. Thermo-mechanical properties and final morphology of these cured blends have been also investigated.

Experimental

Materials and sample preparation

The epoxy precursor used was diglycidyl ether of bisphenol A (DGEBA), supplied by Ciba under the commercial name of Araldite F. Its epoxy equivalent mass was 178 g eq^{-1}, which was measured by chemical titration of the end groups. The linear PVPh polymer (from Polysciences) was characterised in a previous work [16]. Its number average molecular mass was 1500 g mol^{-1} with a polydispersity index of 2. As reaction initiator and catalyser, we used 2-methylimidazole (2MI) of 98% purity, manufactured by Sigma Aldrich. Acetone Panreac QP (0.3% water content) was used as solvent.

DGEBA/PVPh mixtures were prepared by two different methods, by solution in acetone and by thermal homogenisation. The first procedure consisted on mixing appropriated amounts of acetone solutions of each component (at 10 mass%). Then, the resultant solution was dried under vacuum at 50°C until constant mass. The same treatment was applied to the solutions cast on glass slides in order to observe its opacity or transparency. This procedure allowed obtaining uncured mixtures at low temperatures, avoiding the possible reaction between the components. These samples were used to determine the homogeneity of initial DGEBA/PVPh blends with different thermoplastic content, from 10 to 90 mass% PVPh, by DSC measurements and visual analysis. The thermal procedure was used to prepare DGEBA/PVPh/2MI samples. Binary DGEBA/PVPh mixtures were mixed at 90°C during one hour. Then, the imidazole was added in a 2 or 5 mass% with regard to DGEBA mass. The resultant mixture was stirred during 3 min at 90°C. Immediately after, it was transfer into DSC aluminium pans, to study the curing process, or into a steel mould, where thermal curing treatment was applied. The walls of mould were previously treated with an anti-adherent demould agent, Frekote NC44. Afterwards the mould was introduced into heating plates for curing. The cure condition, 180°C during one hour, was established in accordance to previous studies [11]. By this method, DGEBA/PVPh/2MI blends having different amounts of PVPh, from 5 to 40 mass%, have been prepared together with the unmodified resin, adding different 2MI percentage, 2 or 5 mass%. The ratio of epoxy groups (from DGEBA) with regard to phenol equivalents (from PVPh) was 12.8, 6.1, 2.7, 1.6 and 1.0 for the blends with 5, 10, 15, 20, 30 and 40 mass% PVPh, respectively.

Methods

Differential scanning calorimetry (DSC) measurements were carried out in a Mettler mod. 821 apparatus, calibrated with indium and zinc. The reaction enthalpy (ΔH) was measured in scanning mode, from 30 to 250°C, at two different heating rates 10 and 20°C min^{-1} under nitrogen atmosphere. In principle, high heating rates enhances the detection of glass transitions by DSC while low rates are more suitable to measure reaction enthalpies. This first scan was followed by a rapid cooling and a second scan was done at 20°C min^{-1} in order to determine the glass transition temperature (T_g) of the blends. The analysis of initial homogeneity and possible chemical reaction of binary DGEBA/PVPh blends was done by three heating DSC scans at 20°C min^{-1}, from –60 to 100°C for the first scan and to 300°C for the following scans. T_g was taken at the middle point of the heat capacity change.

Dynamic mechanical thermal analysis (DMTA) was performed in dual cantilever bending mode using a DMTA V Rheometric Scientific instrument. All the experiments were done at 1 Hz frequency, by bending deformation, scanning from 0 to 200–250°C using a heating rate of 2°C min^{-1}. The maximum of tan δ *vs.* temperature plots was used to identify the α relaxations associated to the glass transitions. Two scans have been performed for each sample, whose dimensions were 35·12·1.5 mm.

To determine the network structure and the molecular interactions involved on cured DGEBA/PVPh/2MI blends, two different techniques were used Fourier-transform infrared spectroscopy (FTIR) and solid state ^{13}C nuclear magnetic resonance (NMR). In both cases, the sample had to be grinded, obtaining fine powders. For IR measurements, these powders were mixed with dry potassium bromide and pressed on thin disk form. These disks were dried in vacuum at 80°C during one hour. IR spectra were collected in a Nicolet Magna IR-750 apparatus, at 2 cm^{-1} resolution in a wavenumber range 400–4000 cm^{-1}. NMR solid-state cross-polarization/magic angle spinning were performed on a Varian–400 spectrometer. The measurement conditions were the same applied by Woo *et al.* [15]. NMR spectrum of neat DGEBA was obtained in liquid state on a Bruker 300 MHz apparatus. ^{13}C chemical shifts were externally referenced to tetramethylsilane.

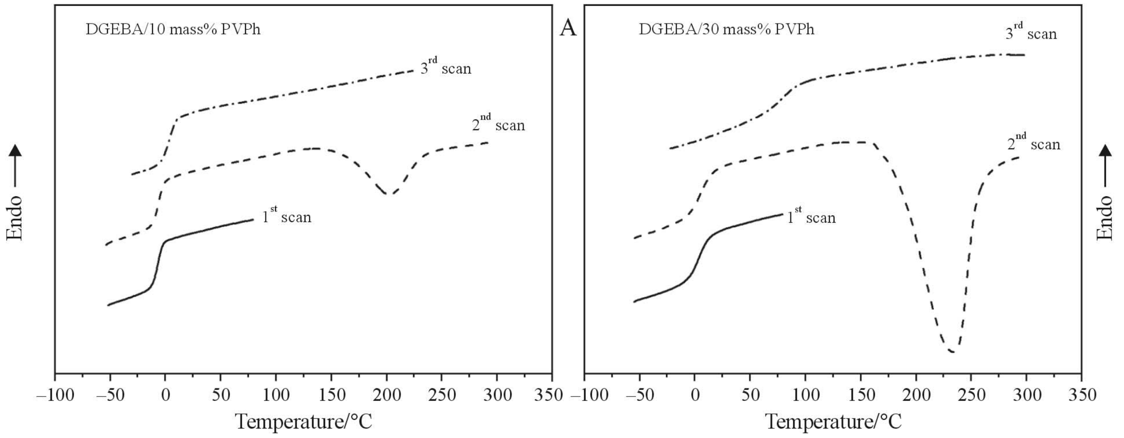
Blends morphology was examined by scanning electron microscopy (SEM, Phillips XL30). The fracture surfaces of the samples were coated with gold by vapour deposition using a vacuum sputter.

Results and discussions

Binary DGEBA/PVPh blends

The miscibility of binary DGEBA/PVPh blends was studied on samples obtained by casting from acetone solutions. At room temperature, the blends appear transparent over the whole composition range, indicating apparent miscibility of the system. Glass transition analysis was carried out by DSC to confirm it, because a miscible polymer blend must present only one T_g, whose value has to be intermediate between the T_gs of the pure components [1, 2]. Taking into account that phenol-epoxy reaction occurs above 130°C [15], the first DSC scan was done from –60 to 100°C, in order to measure the T_g of unreacted mixtures. Then, two following scans were done from –60 to 300°C to study the blend T_g evolution when the components react. Figure 1 shows the DSC scans and the obtained results. For all blends, only a single T_g was detected, which can be associated to DGEBA/PVPh miscibility. Unfortunately, it could not be confirmed the absence of PVPh T_g in the blends, because when the samples were heated near to PVPh T_g, the epoxy/phenol reaction occurred. For each composition, the first and second scans gave the same T_g values. These values are quite low compared to those calculated through Fox equation ($1/T_g=w_1/T_{g1}+w_2/T_{g2}$) [17] for 'ideal' miscible polymer blends, whose predictions are also represented in Fig. 1.

Miscible blends with strong interactions between components usually present positive deviations from Fox rule [18–20]. The epoxy groups of DGEBA could interact through hydrogen bonds with the hydroxyl groups of PVPh. The T_g–composition relationship obtained indicates that this interaction must be very weak. On the other hand, it is well known that neat PVPh presents a high self-association [21].



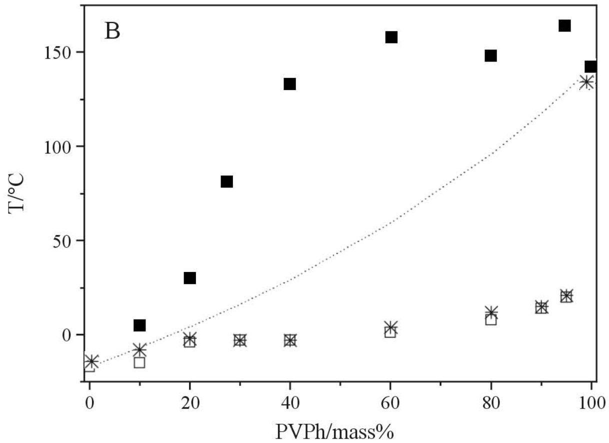


Fig. 1 DSC results of DGEBA/PVPh blends: A – DSC scans for blends containing 10 and 30 mass% of PVPh, B – T_gs measured during the first (□), second (∗) and third (■) scans plotted *vs.* PVPh percentage, together with Fox rule predictions (······)

The rupture of this association when it is mixed with epoxy pre-polymer can explain the observed lowering of the blend T_g from the Fox rule. Blends prepared by thermal homogenisation at 90°C behave similar than the solvent cast. In conclusion, the binary DGEBA/PVPh samples, independently of used preparation method, seem homogenous although they must be close to the solubility limit.

The second scans show a great exothermic peak (Fig. 1), centred at 240°C, which can be associated to epoxy-phenol reaction according to Woo results [15]. In the epoxy/phenol systems, two reactions can occur. First epoxy and phenol groups reacts generating secondary hydroxyl group, which can react with remaining epoxy groups [8, 9]. Both reactions give rise to crosslinked structure.

The third DSC scan gives higher T_g values than the previous ones, indicating that the reaction occurred during the second scan increases the blend T_g. These T_g values strongly depends on thermoplastic concentration. At PVPh content lower than 40 mass% PVPh, the T_g slowly increases with the thermoplastic content and never overcomes 70°C. At 40 mass% PVPh, a great increment in T_g is detected, and for higher PVPh concentrations the T_g almost remains constant, close to 150°C. It is worthy to note that the composition 40 mass% PVPh corresponds to the stoichiometric epoxy/phenol ratio. Therefore, it is likely to assume that, for this composition, the epoxy-phenol reaction reached the maximum conversion. Higher PVPh content should not increase the crosslinking neither the system T_g as already it has been observed.

The T_g of DGEBA/PVPh networks slightly overcome the T_g value of neat PVPh, so using DGEBA as crosslinking agent for PVPh would generate a new material with similar T_g but not flow properties as main advantage.

Curing study of DGEBA/PVPh/2MI

As DGEBA/PVPh blends with low thermoplastic content (<40 mass% PVPh) do not reach high T_g values, even heating at high temperatures, we have studied the tertiary system DGEBA/PVPh/2MI. In this system, two possible reactions can occur; epoxy-phenol reaction and epoxy-epoxy homopolymerisation, both catalysed by imidazole [3–10]. Figure 2 shows the curing thermograms obtained by DSC in dynamic mode for mixtures of DGEBA with different PVPh percentages and 5 mass% 2MI, obtained at a heating rate of 10°C min^{-1}.

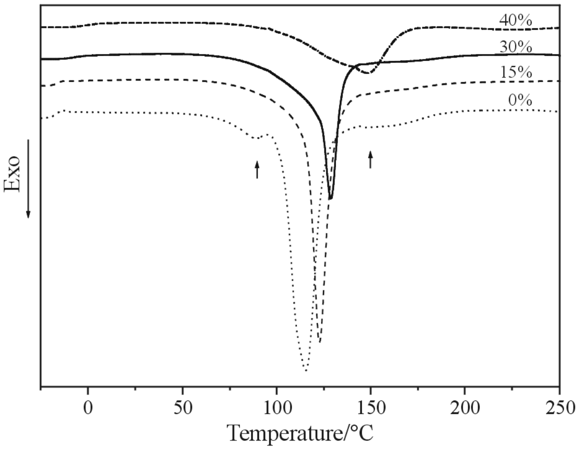


Fig. 2 DSC curves showing curing exotherm for DGEBA/PVPh/5 mass% 2MI with different PVPh content (0, 15, 30 and 40 mass%)

The curve registered for DGEBA/2MI mixture, without thermoplastic (0%), must correspond on epoxy homopolymerisation process. The multiple exotherm peaks observed are characteristic of epoxy etherification reaction initiated by 2-substituted imidazole [4, 5]. The small peak at lower temperature is attributed to the adduct formation step. An imidazole molecule reacts with an epoxy group, forming the 1:1 adduct, which is able to react after with other second oxirane ring, obtaining the 1:2 adduct [4, 5]. The main peak is associated to epoxy O-etherification reaction, i.e. the reaction of anion alkoxy from 1:2 adduct with epoxy groups, forming the network. The third peak at high temperature has been associated to two different processes. Heise and Martin [5] have attributed it to epoxy polymerisation via OH-etherification, i.e. the reaction of epoxy with secondary hydroxyl groups without catalyst. Alternatively, Ooi *et al.* [4] associated it to imidazole regeneration, either by N-dealkylation or β-elimination.

The presence of PVPh causes a broadening and a shift of the main peak to higher temperature and the secondary peaks seem disappear as the PVPh content increases. The shift of mean peak at higher temperature when the phenol concentration increases has been already observed by Lin *et al.* [8] for other epoxy-phenol systems and means a change of the reaction mechanism. The initiation reaction step depends on the epoxy/phenol ratio. When the epoxy concentration is high, the formation of epoxy-imidazole adducts is enhanced. The increase of phenol concentration causes that the main initiation reaction becomes the generation of epoxy-phenol-imidazole complexes. Therefore, for DGEBA/2MI system, the main reaction is the epoxy O-etherification through epoxy/imidazole adducts. But, for DGEBA/PVPh/2MI system, the reaction mechanism changes and the main reaction becomes phenol-epoxy etherification through epoxy-phenol-imidazole complexes. The peak shift at higher temperature indicates that the epoxy-phenol reaction through complexes must have higher activity energy than epoxy etherification through adducts. It can be appreciated that, for DGEBA with 40 mass% PVPh, the exothermic peak is localised close to 150°C when 5 mass% 2MI is added. This temperature is lower than the corresponding to the exotherm peak observed in non-catalysed mixture (240°C).

Table 1 collects the reaction enthalpy (ΔH) measured by DSC at 10 and 20°C min^{-1} for all studied compositions. The enthalpy values decrease when the PVPh content increases. For the neat epoxy resin (0% PVPh), the results are in agreement with the previously reported for the epoxy etherification reaction initiated by imidazole, 88 kJ epoxy eq.$^{-1}$ [4, 5]. The reported enthalpy for phenol-epoxy reaction is close to 80 kJ epoxy eq.$^{-1}$ [8, 9]. However, the obtained value for the DGEBA/PVPh/2MI blends with epoxy/phenol stoichiometric ratio (40 mass % PVPh) is quite lower. This reflects that some phenol groups have not reacted in the blends cured during DSC scans. The phenol groups belong to the PVPh polymer chains and therefore some of them can be inaccessible to the epoxy reaction, because of steric hindrances.

Figure 3 shows the T_g values obtained for DGEBA/PVPh/2MI system, which were measured by DSC. All the cured samples present two different T_gs, named as T_{g1} and T_{g2}. The higher T_g (T_{g2}) is close to 150°C and can be associated to the cured network. Therefore its value can give an idea about the crosslinking degree of the studied system. A light increase of this network T_g is observed at increasing the thermoplastic content. Unfortunately, not great differences are detected, due to the high width of the transitions. Due to this high width, the T_{g2} has been analysed measuring the onset and offset of the transition. Broad glass transitions were also observed by Woo *et al.* for uncatalysed DGEBA/PVPh samples [15] and can be attributed to micro-heterogeneities associated with the polymeric structure of the reactive phenol used. Moreover, as it was discussed above, two different reactions, epoxy-epoxy etherification and epoxy-phenol reaction, can take place generating crosslinking zones with different free volume and different mobility.

The DGEBA/PVPh samples catalysed with 2 mass% 2MI present a similar behaviour to the ones obtained with 5 mass% 2MI. Nevertheless, the values of the network T_g (T_{g2}) are quite higher, close to 170°C, and the transitions are not so broad. The increase of imidazole concentration must cause an increase of the initial reactive anions concentration (adducts and complexes), enhancing the initiation against the propagation and giving rise to lower T_{g2} epoxy networks.

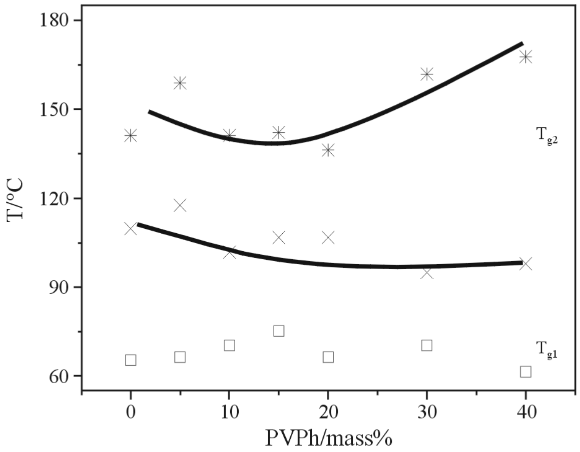


Fig. 3 T_gs of cured DGEBA/PVPh/5 mass% 2MI blends. T_{g1} was measured in the middlepoint (□) while T_{g2} was determined by the onset (∗) and offset of the transition (×)

Together to the glass transition at high temperature (T_{g2}), the studied system presents a minor transition (T_{g1}), whose value does not depend on the blend composition (Fig. 3). T_{g1} is close to 45 and 70°C for DGEBA/PVPh systems catalysed with 2 and 5 mass% 2MI, respectively. This secondary transition has been only reported before by Williams *et al.* [3] for diepoxide systems initiated by tertiary amines. They associated it with regions of different crosslinking degree. They probed that a microgel phase appears early in the polymerisation before macroscopic gelation takes place, giving rise to cured heterogeneous networks. This behaviour was explained by the presence of an intermolecular chain transfer reaction, which liberates reactive alkoxy anions. Then they can react with pendant epoxy groups belonging to its original chain. If this situation is repeated, a local network (microgel) will be produced. In this work, we have found that this intramolecular reaction mechanism, proposed by epoxy etherification, occurs also in epoxy/phenol systems.

Table 1 Reaction enthalpy for DGEBA/PVPh/5 mass% 2MI blends measured by DSC at two heating rates (ν)

	ΔH/kJ epoxy eq.$^{-1}$						
ν/°C min^{-1}	PVPh/mass%						
	0	5	10	15	20	30	40
10	86.2	79.6	72.9	76.6	77.6	72.5	66.7
20	90.2	85.2	79.5	75.0	74.2	74.6	71.5

Network structure analysis of cured blends

FTIR and NMR analysis were done to explore the molecular structure of the cured DGEBA/PVPh/2MI blends. Figure 4 shows the ^{13}C-NMR spectra. The DGEBA spectrum was obtained in solution while the rest of spectra were measured with solid state samples. This explains the different resolution and width of the resonance peaks. The assignment of resonance peaks was made following the results previously reported by Woo *et al.* [15] and it is summarized in the Table 2.

The peaks assigned to epoxy groups, at 50 and 45 ppm, in the neat DGEBA spectrum, do not appear in the DGEBA/PVPh/2MI blends spectra, independently of the composition. This means that, in all cases, the epoxy conversion reached is very high. The peak corresponding to phenol carbon, at 146 ppm, observed in the neat PVPh spectrum, disappears in the blends spectra. This fact together with the observed

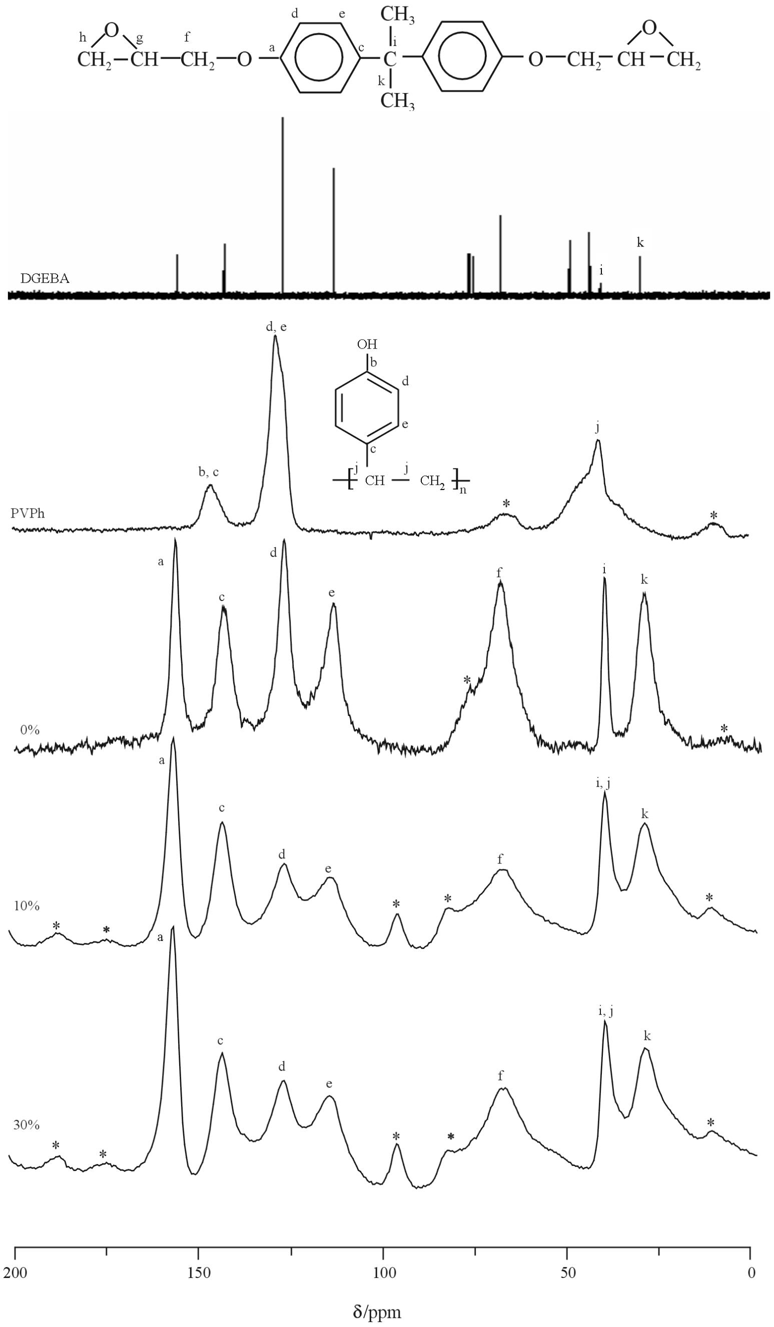


Fig. 4 ^{13}C-NMR spectra for neat DGEBA, neat PVPh and cured DGEBA/PVPh/5 mass% 2MI with different PVPh content (0, 10 and 30 mass%)

increase of the peak intensity, associated to aromatic ether carbons (156 ppm), indicates that the most of phenol groups of PVPh have reacted with epoxy ones.

FTIR spectra were obtained for neat DGEBA, neat PVPh and DGEBA/PVPh blends cured with 5 mass% 2MI having the following PVPh percentages 0, 10, 20, 30 and 40 mass%. Figure 5 shows the FTIR spectra for the hydroxyl region (3700–3100 cm^{-1}) (Fig. 5A) and epoxy groups region (930–900 cm^{-1}) (Fig. 5B). Not great differences are observed on the blends spectra, confirming the high similarity of the samples.

The epoxy groups of neat DGEBA exhibits an absorbance band centred to 914 cm^{-1}. This band remains at the same frequency in the blends although its intensity noticeably decreases no finding difference with the PVPh content. Therefore, the final epoxy conversion in all the blends remains approximately constant, independently of the composition, and its value must be very high. These evidences support the RMN and DSC results. In the hydroxyl region some differences can be observed between the neat components and the blends. In the neat PVPh spectrum, a broad band centred close to 3355 cm^{-1} appears which is assigned to a wide distribution of hydrogen bonded phenol groups [15]. This reveals the high PVPh self-association. In the cured DGEBA/PVPh/2MI blends, the shoulder peak occurs at the same frequency, but the broad band of hydrogen bonded hydroxyl groups is shifted to higher frequency (3445 cm^{-1}) independently of the blend composition. Similar behaviour was observed when uncatalysed samples were heated at 177°C [15]. This high shift means that the epoxy-phenol reaction has occurred. The absence of residual band at 3355 cm^{-1} could indicate that almost all PVPh phenol groups have reacted, in agreement with RMN results.

An absorbance shoulder band at 3565 cm^{-1} is attributed to free or non-hydrogen bonded hydroxyls. In all blends, the integrated area of whole hydroxyl

Table 2 Assignments of the ^{13}C chemical shifts for neat DGEBA, neat PVPh and DGEBA/PVPh/5 mass% 2MI blends

Peak	δ(ppm)	Assignment	Spectra where appears the peak
a	156	Aromatic C–O	DGEBA, blends
b	146	Aromatic C–OH	PVPh
c	142	Aromatic quaternary carbon	DGEBA, PVPh, blends
d	127	Aromatic CH	DGEBA, PVPh, blends
e	114	Aromatic CH	DGEBA, blends
f	68	Aliphatic C–O	DGEBA, blends
g	50	Epoxide CH	DGEBA
h	45	Epoxide CH_2	DGEBA
i	40	Aliphatic quaternary carbon	DGEBA, blends
j	40	Aliphatic CH_2, CH	PVPh, blends
k	30	CH_3	DGEBA, blends

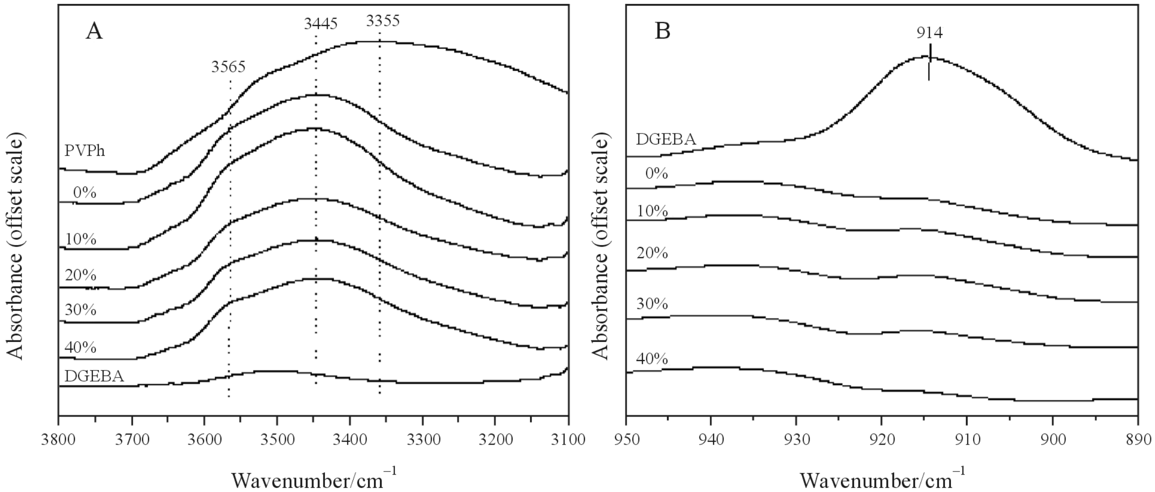


Fig. 5 FTIR spectra for neat DGEBA, neat PVPh and cured DGEBA/PVPh/5 mass% 2MI blends with different PVPh content (0, 10, 20, 30 and 40 mass%): A – absorbance region of hydroxyl groups and B – epoxy band

band (bonded and free) remains almost constant. This can be explained taking into account that the epoxy-phenol reaction generates one aliphatic hydroxyl group per each reacted phenol group and that at the cured temperature, 180°C, the aliphatic hydroxyl-epoxy reaction is not favoured.

Morphology and final properties of cured blends

As it has been discussed above, the glass transitions of the cured blends, determined by DSC (Fig. 3), are quite broad. In order to have better determination of the network relaxations, DMTA measurements were performed. Figure 6 shows the loss tangent (tanδ) isochrones (1 Hz) *vs.* temperature for neat epoxy network homopolymerised with 2 and 5 mass% 2MI (Fig. 6A) and for DGEBA/PVPh/5 mass% 2MI blends (Fig. 6B).

A small maximum in tanδ is observed around 80°C in all cases, in agreement with the secondary T_g (T_{g1}) observed by DSC. The main α relaxation appears in the 150–220°C range. As can be seen, the tanδ peak of the neat epoxy resin catalysed with 2 mass% 2MI is narrower than the one homopolymerized with 5 mass%. In fact, the relaxation of epoxy network crosslinked with 5 mass% 2MI takes place in a broad temperature range, compared with the epoxy resins cured with typical crosslinking agents, like diamines [22]. The increase of the transition width generally indicates a higher dynamic heterogeneity; according to the coupling model broad transitions are related to higher cooperativity between the molecules [23]. The tanδ maximum appears at lower temperature when the 2MI percentage increases, as it is illustrated in Fig. 6A for the neat system. DSC T_gs displayed the same tendency and it reveals that the increase of imidazole concentration that enhances the initiation against the propagation step provides networks that relax at lower temperatures [4]. This behaviour was also observed for cured epoxy blends with 5 mass% PVPh content. However, the blends with higher PVPh content (≥10%) present the opposite behaviour. Figure 6B illustrates how the increase of PVPh percentage shifts the tanδ peak at higher temperatures. Considering that in all blends most of phenol groups have reacted, and the high functionality of PVPh (one phenol per monomer unit), the increase of thermoplastic content generates networks with higher crosslinking degree, which relax at higher temperatures. This effect seems to prevail over the imidazole concentration influence.

It is worthy to note the high temperature of tanδ peak in DGEBA/PVPh blends, reaching 202 and 206°C for 30 and 40 mass% PVPh, respectively. For these compositions, the storage modulus in the glassy state, E_G, remains almost constant on a broad temperature range, from $1.2\cdot10^9$ GPa at room temperature to $1\cdot10^9$ GPa at 130–150°C.

The morphology of blends was observed by SEM. Figure 7 shows the micrographs of fractured surfaces of DGEBA/PVPh/5 mass% 2MI samples. For all compositions, the observed morphology was quite homogeneous and free of any discernible domains. Therefore, the two T_gs detected by DSC and the two α relaxations observed by DMTA are not originated by neat separated phases, in domains ≥1 μm. It is likely that both transitions have its origin on regions with different crosslinking degree. Similar morphology was observed when the fractured samples were before immersed into tetrahydrofurane (a good solvent for PVPh) and stirred during 24 h. This confirms that the PVPh is not phase separated, in accordance with the results above presented.

The appearance of the fractured surfaces changes with the PVPh content (Fig. 7). At low PVPh percentages, the micrographs exhibit the typical flat

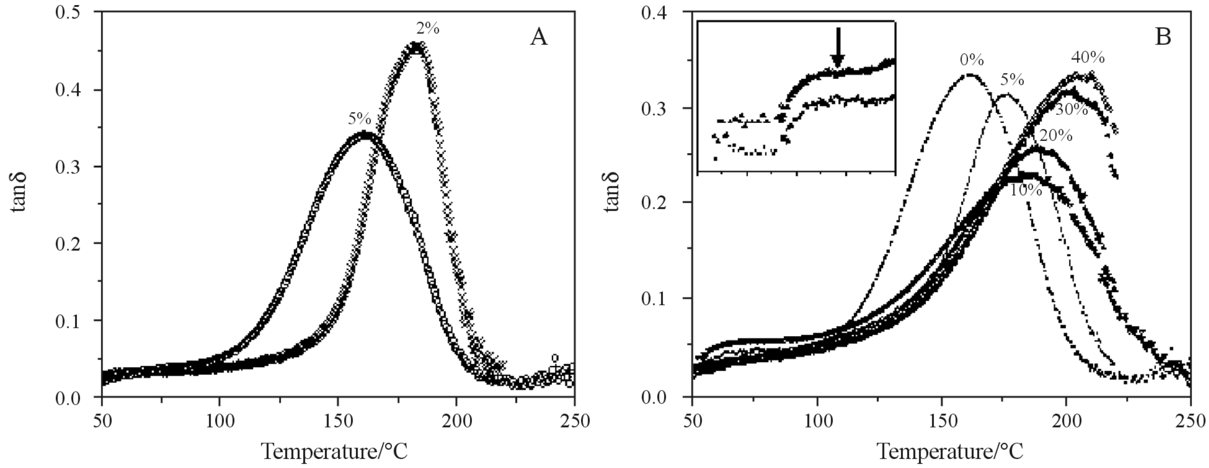


Fig. 6 DMTA isochrones at 1 Hz, tanδ *vs.* temperature plots: A – DGEBA cured with 2 and 5 mass% 2MI and B – DGEBA/PVPh/5 mass% 2MI blends with different PVPh contents (0, 5, 10, 20, 30 and 40 mass%)

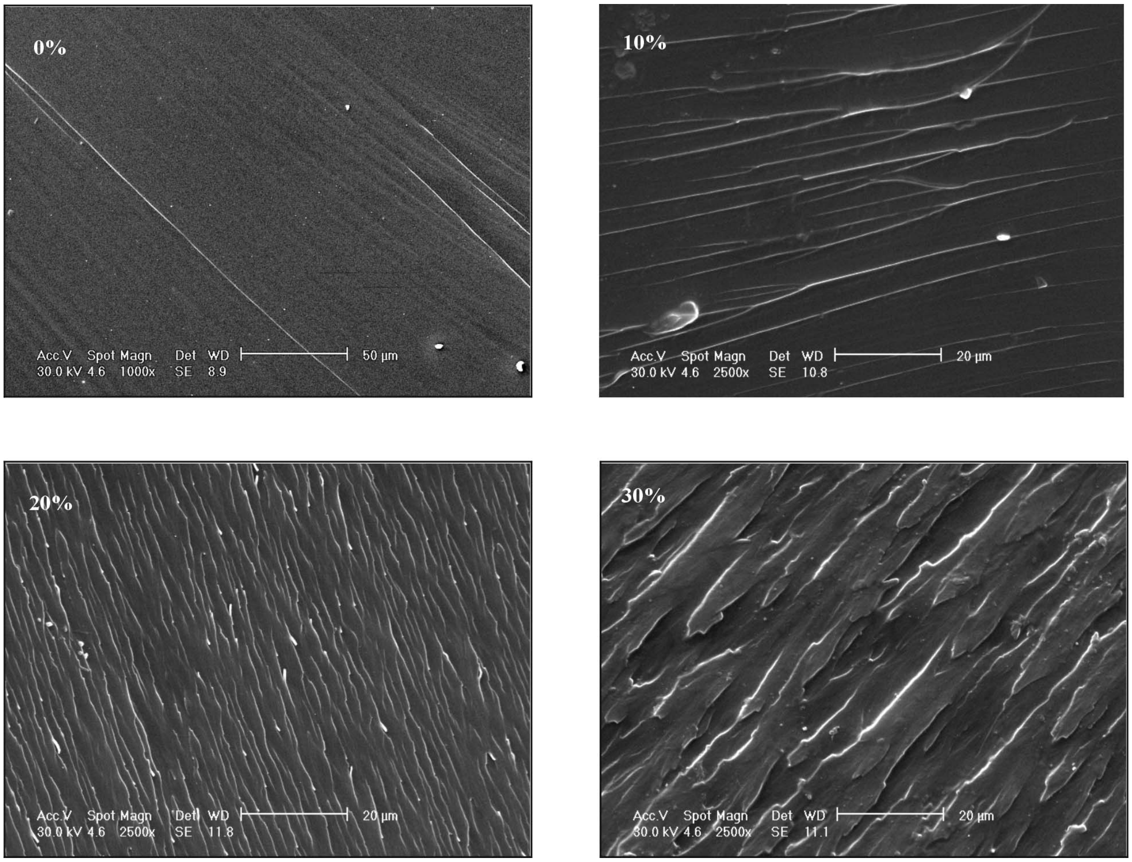


Fig. 7 ESEM micrographs for cured DGEBA/PVPh/5 mass% 2MI blends with different PVPh content (0, 10, 20 and 30 mass%)

and brilliant surface characteristic of brittle materials. When the thermoplastic content increases, the fracture surfaces become rougher. There are deviations and branches of the crack front. In the micrographs collected for the cured blend with 40 mass% PVPh, the crack front branches off and lines with different roughness appear. This behaviour indicates that the fracture mechanism changes, becoming the samples less brittle.

Conclusions

Binary DGEBA/PVPh blends behave as miscible, showing a single low T_g and transparency. Heating up 180°C, the mixtures with high PVPh content reach T_g values close to 150°C. However, for PVPh percentages lower than 40 mass%, it is necessary the introduction of a catalyser/initiator agent, as imidazole, to obtain networks with high T_gs. In all cases, the final blends are homogeneous, without SEM noticeable separated phases. DGEBA/2MI and DGEBA/PVPh/2MI samples present a secondary glass transition, at low temperature (45–70°C), which is associated to regions with different crosslinking degree probably originated by intermolecular chain transfer reaction.

The epoxy homopolymerisation is the main reaction at low PVPh contents, while for PVPh percentages higher than 20 mass%, the epoxy-phenol reaction prevails. The increase of imidazole concentration to 5 mass% enhances initiation *vs.* propagation, giving rise to DGEBA/PVPh networks with lower T_g and lower α relaxation temperature than the corresponding with 2 mass% 2MI. According to the solid state ^{13}C-NMR and FTIR spectra, almost all PVPh phenol groups were reacted.

Cured blends present a broad main T_g, indicating network heterogeneity. The increase of PVPh percentage raises the T_g values and α relaxation temperatures of the networks. The high conversion reached and the high functionality of PVPh explains it. The addition of 30 and 40 mass% PVPh modifies the fracture mechanism becoming the samples less brittle, which are homogeneous and present high α-relaxation temperature, close to 200°C.

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