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MECHANICAL PROPERTIES AND MORPHOLOGY OF EPOXY/POLY(VINYL ACETATE)/POLY(4-VINYL PHENOL) BROMINATED SYSTEM

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Diglycidyl ether of bisfenol-A (DGEBA)/poly(vinyl acetate) (PVAc)/poly(4-vinyl phenol) brominated (PVPhBr) ternary blends cured with 4,4'-diaminodiphenylmethane (DDM) were investigated by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and scanning electron microscopy (SEM). Homogeneous (DGEBA+DDM)/PVPhBr networks with a unique T_g are generated. Ternary blends (DGEBA+DDM)/PVAc/PVPhBr are initially miscible and phase separate upon curing arising two T_gs that correspond to a PVAc-rich phase and to epoxy network phase. Increasing the PVPhBr content the T_g of the PVAc phase move to higher temperatures as a consequence of the PVAc-PVPhBr interactions. Different morphologies are generated as a function of the blend composition.

Keywords: *epoxy, glass transition, morphology, poly(vinyl acetate), poly(4-vinyl phenol) brominated, ternary blends*

Introduction

Epoxy/thermoplastic binary blends have been widely studied in the past decade because they offer the possibility of generating materials with improved properties. The initial mixture consists of a thermoplastic dissolved in the epoxy resin precursor (epoxy monomer+curing agent). On curing, the blends phase separate, giving rise to different morphologies as a function of the thermoplastic content, and the mechanical properties of the cured system are related to the morphology [1–13]. However there are few studies dealing with ternary blends involving an epoxy thermoset and two thermoplastic linear polymers. Most of the studies use two non miscible thermoplastics [14–19] and double phase separation takes place on curing the ternary blend. The addition of block-copolymers that interact with the homopolymers has been used to modify the morphology [19]. The modification of epoxys by the simultaneously addition of two thermoplastics which are miscible together has been scarcely reported [20].

In previous works [10–13] we have reported the behaviour of epoxy/polyvinyl acetate (PVAc) blends cured with diamines. The obtained biphasic materials show different morphologies as a function of PVAc content and present higher toughness than unmodified epoxy thermoset [7]. However, when the PVAc content overrides 10 mass% the elastic modulus of the material decreases, this is related to the change in morphology which becomes inverted (epoxy domains surrounded by PVAc).

In this work, we study ternary blends formed by an epoxy resin and two thermoplastics. The epoxy thermoset is based on diglycidyl ether of bisphenol A (DGEBA) and 4,4'-diaminodiphenylmethane (DDM) is used as curing agent. The thermoplastics selected are PVAc and poly(4-vinyl phenol) brominated (PVPhBr). PVPhBr is a high T_g polymer used as flame retardant additive. In a previous work we have reported that non reactive binary blends of PVPhBr with PVAc are miscible in the whole composition range [21], this is due to the hydrogen bonding between hydroxyl groups of PVPhBr and carbonyl groups of PVAc. It is known that phenols are reactive to the epoxy groups, consequently polyvinyl phenols are used as substitutes of novolac resins in epoxy formulations. Moreover it has been demonstrated that poly(4-vinyl phenol) reacts with DGEBA forming homogeneous networks [22, 23]. Therefore it is expected that the morphology and properties of the cured ternary epoxy/PVAc/PVPhBr would be determined by two factors: the interactions between thermoplastics and the reactivity of PVPhBr to epoxy. The aim of the present study is to analyze the influence of the addition of the PVPhBr on the mechanical properties and morphologies generated upon curing epoxy/PVAc/PVPhBr which will be compared to epoxy/PVAc and ep-

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oxy/PVPhBr binary systems. Differential scanning calorimetry (DSC), infrared spectroscopy (FTIR), dynamic-mechanical thermal analysis (DMTA) and scanning electron microscopy (ESEM) have been used.

Experimental

Materials and blend preparation

The epoxy prepolymer, DGEBA, was supplied by Uneco S.A., Spain under the commercial name of Araldit F. The number average relative molecular mass M_n=380 g mol^{-1}. The curing agent, DDM, was manufactured by Sigma-Aldrich (97 mass%). PVPhBr was obtained through bromination of PVPh of M_n=3·10^3 g mol^{-1} and polydispersity index=2, it contains 50 mass% of bromine, that is, an average of 1.5 bromine atoms per each repeating unit. Poly(vinyl acetate) has M_n=8.6·10^4 g mol^{-1} and polydispersity index=1.9, both thermoplastics were purchased from Polysciences. DGEBA and DDM were used with a stoichiometric ratio amino-hydrogen to epoxy. In order to prepare ternary blends (epoxy/PVAc/PVPhBr), PVAc was first solved in DGEBA prepolymer at 100°C, then PVPhBr was solved at 80°C to prevent previous phenol-epoxy reaction, 5 min were enough to get complete solution. Finally DDM was solved at 80°C during 2 min, at this stage all the mixtures were transparent, thus indicating miscibility.

For DSC experiments 8–15 mg of these mixtures were placed into DSC aluminium pans. To prepare specimens for DMTA and SEM measurements the mixtures were poured into preheated moulds at 120°C, degassed for 3–4 min and cured under atmospheric pressure following the schedule: 2 h at 120°C, 30 min to rise from 120 to 180°C and 30 min at 180°C. After curing the mould was allowed to cool gradually to room temperature before being removed from the oven. Binary epoxy/PVAc and epoxy/PVPhBr blends were obtained in a similar way. The thermoplastic percentages studied were 0–20 mass% of PVAc, 0–10 mass% of PVPhBr, the overall thermoplastic content never exceeded 30 mass%.

Methods

DSC measurements

Curing reactions were examined by differential scanning calorimetry using a Mettler Toledo mod.822e calorimeter. Glass transition temperatures, T_g, and heats of reaction were determined. T_gs were taken as the midpoint of the heat capacity change. All measurements were done at a heating rate of 20°C min^{-1}, under nitrogen atmosphere. The instrument was calibrated with indium and zinc. Samples of 8–15 mg were sealed in aluminium pans.

ESEM measurements

Environmental scanning electron microscopy (ESEM) mode was used to study the morphology of the cured samples. A Phillips XL30 instrument was employed with a beam energy of 20 kV, verifying that this did not produce severe damage on the samples. The water vapour pressure was 0.6–0.7 Torr, that corresponds to a relative humidity of ~5%.

IR measurements

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna-IR 750 spectrometer in transmission mode (64 scans, resolution 4 cm^{-1}). Samples were ground to a fine powder and pressed into a pellet.

DMTA measurements

Dynamic mechanical thermal analysis of cured samples was performed in dual cantilever bending mode using a DMTA V Rheometric Scientific instrument. All measurements were done at 1, 2, 6, 10, and 50 Hz frequency, with temperature increasing from 25 to 250°C at a heating rate of 1°C min^{-1}. The maxima on tanδ-temperature and on E''-temperature curves were determined to identify the α-relaxations associated to the glass transitions.

Results and discussion

Dynamic curing of epoxy/PVPhBr and epoxy/PVAc/PVPhBr blends by DSC

Figure 1 shows the dynamic DSC curves (20°C min^{-1}) of the first scan for neat epoxy (DGEBA+DDM) and for its blends with different amounts of PVPhBr. In all the cases a single exotherm is observed, the onset and peak temperatures are quoted in Table 1 together with the heat of reaction calculated from the peak areas. The incorporation of PVPhBr decreases the onset temperature and shifts the exothermal peak temperatures to lower values. Moreover the peak area decreases as PVPhBr content increases, this is not only a dilution effect due to the increasing PVPhBr content. Thus, when the heats of reaction are referred to the epoxy equivalent, (Table 1) also decrease as the PVPhBr content increases. It is known that phenol groups are reactive to epoxy groups [22], and although the main reaction in this blend is epoxy-amine some phenols of PVPhBr must have reacted during the DSC scan and as a consequence the curing reac-

Table 1 Epoxy(DGEBA+DDM)/PVPhBr blends. Data from DSC exotherm: T_{onset}, T_{peak} and ΔH. T_gs for uncured (T_g^0) and for cured samples during the first scan (T_g^c)

PVPhBr/mass%	T_{onset}/°C	T_{peak}/°C	$-\Delta H$/J g^{-1}	$-\Delta H$/kJ ee^{-1}	T_g^0/°C	T_g^c/°C
0	148	187	467	113	–13	155
2	137	184	440	100	–11	154
5	121	172	420	92	–8	100
10	98	157	330	88	4	130

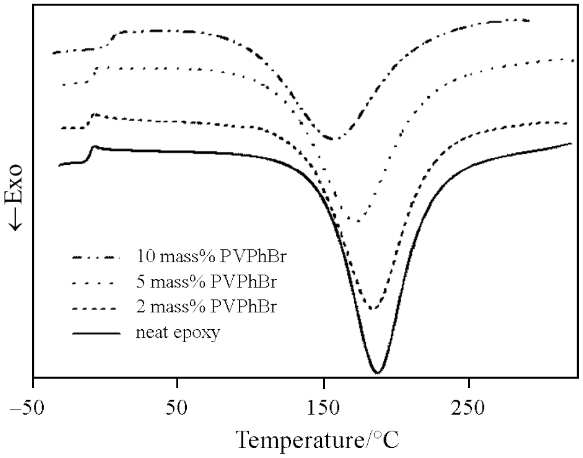

Fig. 1 DSC first scans (20°C min^{-1}) of epoxy/PVPhBr blends containing different amounts of PVPhBr. Curves are referred to the same blend mass

tion is accelerated. In contrast epoxy/PVAc blends present the usual behaviour of epoxy/non reactive thermoplastic blend that is the thermoplastic delays the curing reaction as we have previously reported [10–12].

As can be seen in Fig. 1 a unique T_g is detected in the first DSC scan of the epoxy/PVPhBr mixtures, their values are reported in Table 1. They correspond to the ones expected for miscible unreacted blends, of DGEBA+DDM (T_g~–13°C) and PVPhBr (Tg~150°C), this confirms that no previous reaction has taken place during the blends preparation (80°C). Samples that have been cured during the first DSC scan (–40 to 300°C), were rescanned and for all epoxy/PVPhBr compositions studied, a single T_g at high temperature, T_g^c, was observed (Table 1). From the thermodynamic point of view, as the curing progresses the increase of the molecular mass of the epoxy polymer would provoke phase separation as it was detected in cured epoxy/PVAc system, in which two T_gs corresponding to PVAc phase and to epoxy network phase were detected [12]. Moreover no soluble fraction is present in cured epoxy/PVPhBr samples while in cured epoxy/PVAc the thermoplastic can be removed by solvent etching. This behaviour is an indication that PVPhBr has been chemically incorporated into the epoxy network. It could be observed (Table 1) that samples containing PVPhBr present lower T_g^cs than neat epoxy, reflecting that the generated thermoset reach lower crosslinking density when PVPhBr is present.

A similar DSC study has been carried out for ternary epoxy/PVAc/PVPhBr blends. Before curing, epoxy/PVAc/PVPhBr blends were transparent indicating miscibility, this conclusion was confirmed by DSC measurements because each blend showed a single T_g^0. The T_g^0 values of ternary blends were slightly higher than the corresponding to the binary epoxy/PVPhBr blends (Table 1), this is due to the presence of PVAc (T_g~44°C). The effect of PVPhBr on curing epoxy/PVAc/PVPhBr blends is similar to the effect on curing epoxy without PVAc that was above discussed, i.e. the curing reaction is accelerated when there is PVPhBr. However comparing data of ternary blends with those of binary epoxy/PVPhBr blends having the same content of PVPhBr, the delaying effect of PVAc can be observed, that is, T_{peak}s are slightly higher (5–10°C) than those appearing in Table 1. On the other hand cured ternary blends epoxy/PVPhBr/PVAc are opaque and present two T_gs (T_g~40–60°C and T_g~130–155°C) indicating that these blends are phase separated.

DMTA measurements of cured epoxy/PVPhBr and epoxy/PVAc/PVPhBr blends

Ternary epoxy/PVAc/PVPhBr and binary epoxy/PVAc and epoxy/PVPhBr blends were cured under the schedule: 2 h at 120°C, 30 min to rise from 120 to 180°C and 30 min at 180°C. This protocol conduces to totally cured samples, as it was confirmed by DSC. Binary epoxy/PVPhBr cured blends with 0, 2, 5 and 10 mass% PVPhBr and ternary epoxy/PVAc/PVPhBr having 0, 5, 10 and 15 mass% PVAc and 0, 2, 5 and 10 mass% of PVPhBr were prepared in order to study DMTA behaviour and morphology by ESEM.

In Fig. 2 the loss modulus (E'') and the loss tangent (tanδ) isochrones (1 Hz) for cured epoxy/PVPhBr blends containing different amounts of PVPhBr are plotted *vs.* temperature. As can be seen for all compositions a unique high tanδ peak (~180–184°C) appears, which corresponds to the

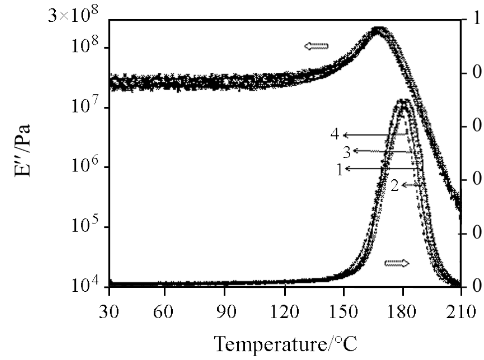

Fig. 2 DMTA scans: E'' and tanδ isochrones (1 Hz) for cured epoxy/PVPhBr blends with different contents of PVPhBr: 1 – 0, 2 – 2, 3 – 5 and 4 – 10 mass%

α-relaxation (T_g) of the epoxy network. A similar pattern has been obtained for isochrones at 2, 6, 10 and 50 Hz, moreover the breadth of the relaxation peaks at the same frequency is similar for all the samples, thus it confirms that binary epoxy/PVPhBr blends do not phase separate on curing and that the blends form a homogeneous phase. The tanδ peak appears at slightly lower temperatures for the higher PVPhBr content, this could indicate that networks of lower crosslinking density are formed. DSC measurements were also carried out and, as usual, the calorimetric T_g values were ~20°C lower than the α-relaxation ones determined from the tanδ peak at 1 Hz. Figure 3 shows micrographs obtained for epoxy/5 mass% PVPhBr, as it was expected, no visible phase domains are observed. Similar results were obtained for other PVPhBr contents which are not shown for brevity. It should be noted that the samples are not modified by etching with methanol. All these samples were transparent and it would be therefore concluded that epoxy/PVPhBr forms homogeneous thermoset i.e. crosslinked networks comprised of networking DGEBA/DDM and linear PVPhBr.

The epoxy network modified with both thermoplastics was investigated subsequently. All cured ternary epoxy/PVAc/PVPhBr blends are non transparent and the dynamic mechanical behaviour is different to

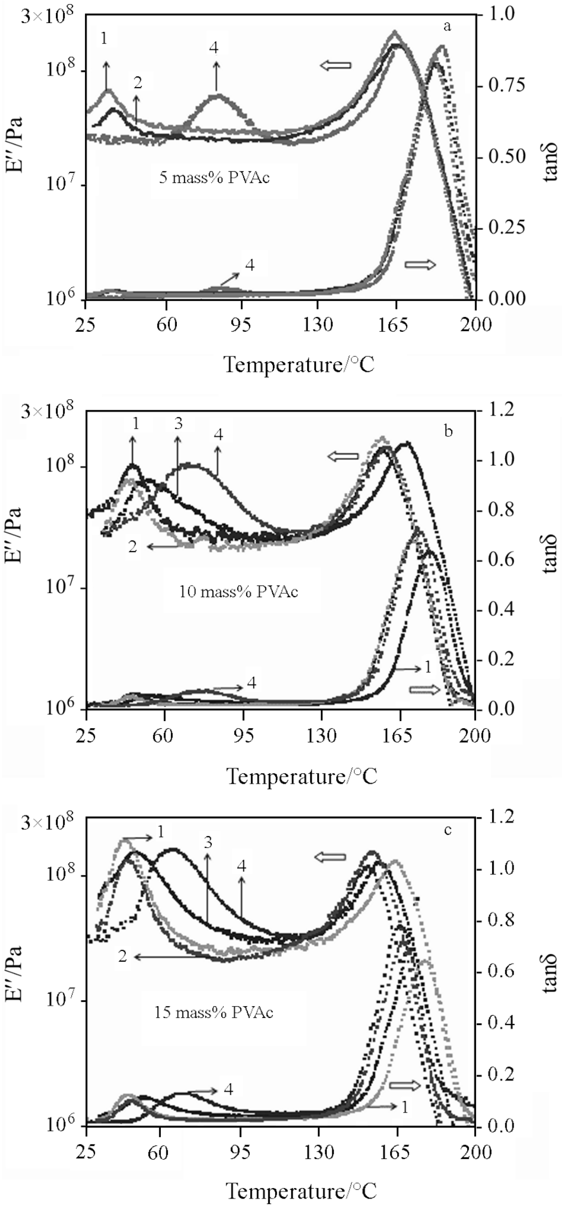

Fig. 4 DMTA E'' and tanδ isochrones at 1 Hz of cured epoxy/PVAc/PVPhBr containing: a – 5 mass% PVAc, b – 10 mass% PVAc and c – 15 mass% PVAc and different PVPhBr percentages: 1 – 0, 2 – 2, 3 – 5 and 4 – 10 mass%

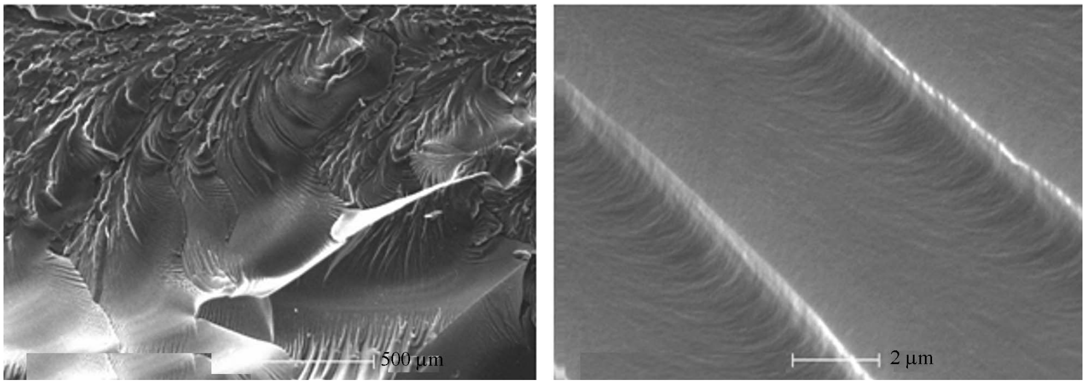

Fig. 3 ESEM of fracture surfaces of cured epoxy/PVPhBr

the one observed in binary blends. Figure 4 presents the dynamic mechanical results for blends containing 5, 10 and 15 mass% of PVAc and different contents of PVPhBr. The blends show two α-relaxations, a pronounced tanδ peak appears (~170–180°C) that corresponds to the epoxy network phase T_g, besides a small tanδ peak is located at ~40–90°C which corresponds to the α-relaxation (T_g) of the PVAc enriched phase. For samples with higher PVAc percentage, the major PVAc content makes it feasible to detect clearly the tanδ peak corresponding to the PVAc phase. The E''-temperature curves show clearly the maxima in the T_g regions.

For all the compositions when PVPhBr is present, the α-relaxation (T_g) of the PVAc rich phase appears at higher temperatures than in epoxy/PVAc blends. This could be due to the interactions of carbonyl groups of PVAc with the phenyl hydroxyls of PVPhBr that remains unreacted. In order to clarify the interactions between polymers, FTIR spectra of cured epoxy/PVAc and cured epoxy/PVAc/PVPhBr samples having different amounts of PVAc and PVPhBr were taken. In all the cases the introduction of PVPhBr makes the C=O band (1739 $\mathrm{cm^{-1}}$) to broaden towards lower frequencies evidencing interactions between both polymers. The broad absorption band at 3700–3100 $\mathrm{cm^{-1}}$ are due to the vibrations of hydroxyls groups. The shoulder at 3548 $\mathrm{cm^{-1}}$ corresponds to free OH and the band centred at 3416 $\mathrm{cm^{-1}}$ represents associated hydroxyls which interact in different ways. In the blends, hydroxyl groups from epoxy and from PVPhBr are present. The presence of PVPhBr in ternary blends increases the ratio associated/free hydroxyls in relation to neat epoxy, to epoxy/PVAc and even to epoxy/PVPhBr binary blends, which is in agreement with the idea that some phenyl hydroxyls of PVPhBr that have not reacted with the epoxy may interact with PVAc.

In Fig. 5, the T_g (tanδ_{maxima}) of PVAc rich phase is plotted as a function of PVPhBr content in epoxy/PVAc/PVPhBr blends for 5, 10 and 15 mass% of PVAc. As can be seen, for each PVAc content there is

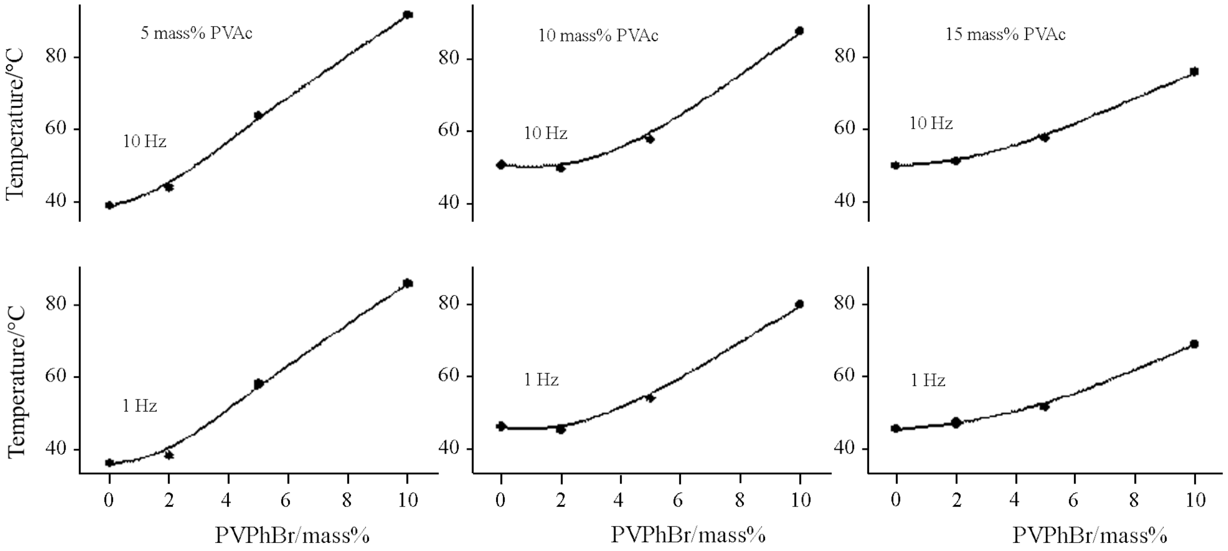

Fig. 5 Temperature of the tanδ_{maxima} (1 and 10 Hz) associated to α-relaxation of PVAc rich phase *vs.* PVPhBr content, for epoxy/PVAc/PVPhBr blends containing 5, 10 and 15 mass% of PVAc

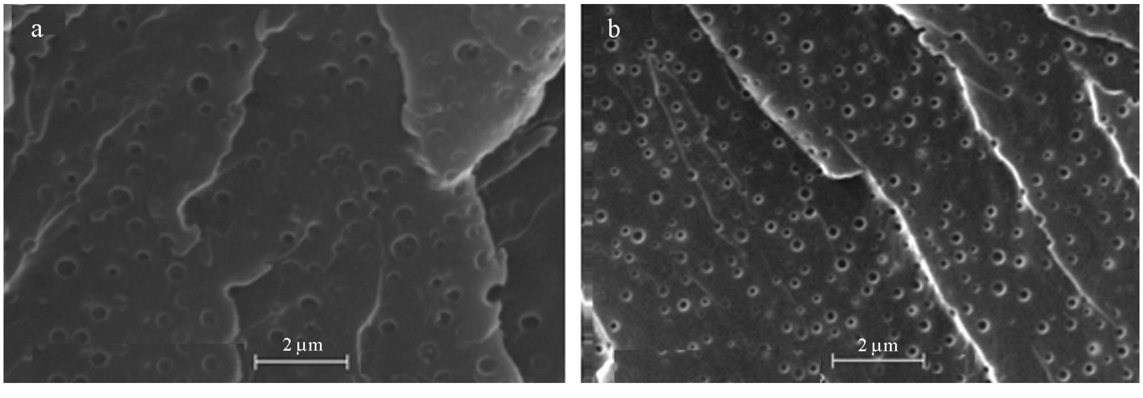

Fig. 6 ESEM micrographs of cured epoxy/PVAc/PVPhBr blends containing a – 5 mass% PVAc/10 mass% PVPhBr and b – 5 mass% PVAc. Fracture surfaces etched with methanol

a correlation between the α-relaxation of the PVAc rich phase and the PVPhBr percentage. Due to the good PVAc-PVPhBr interactions, the PVAc rich phase should contain increasing amounts of PVPhBr, therefore increasing the T_g of this phase. On the other hand comparing curves at the same frequency, it is deduced that as the PVAc content increases, the increment of T_g with PVPhBr content is reduced, meaning that the PVAc rich phase is less rich in PVPhBr as the PVAc content in the blend increases.

It has been reported [20] that the shape and size of E''-temperature curves can give information about the sample morphology. In the blends here studied an increase of the height of E'' maxima of the PVAc phase relaxation occurs as the PVAc content increases (Fig. 4) and it should reflect a change in morphology. Thus for blends containing 5 mass% of PVAc the height of the E'' peak corresponding to PVAc phase is lower than the height of E'' peak associated to the epoxy network relaxation (Fig. 4a). The morphology in these blends is a nodular morphology, as it is illustrated in Fig. 6 small spherical domains of PVAc are dispersed in a continuous epoxy matrix. The presence of PVPhBr (Fig. 6a) reduces the number of spheres and increases their size, this behaviour is opposite to the one observed when block copolymers are added and act as emulsifiers [19]. It should be noted that the fractography has changed being more ductile the samples containing PVPhBr.

On the other hand for blends containing 10 mass% of PVAc the height of both E'' peaks are similar (Fig. 4b) indicating that a change in the morphology is taking place, indeed as we showed in a previous work [12], at that composition the epoxy/PVAc blend starts to become inverted coexisting two types of regions, ones with nodular morphology and the others with inverted morphology (epoxy domains surrounded by PVAc). Figure 7 shows the ESEM micrographs for epoxy/PVAc/PVPhBr containing 10 mass% of PVAc and 10 mass% of PVPhBr. These blends present a co-continuous morphology. The samples were etched with methanol and the micrographs obtained are included in Figs 7c and d. Part of the matrix was solved by methanol then it should be composed by PVAc, confirming the co-continuous morphology. Moreover micrographs obtained at higher magnifications revealed some very small particles dispersed in the epoxy matrix that should be also PVAc-rich phase. Thus the presence of PVPhBr does not modify the critical composition, being the inversion located at 10 mass% of PVAc, but it changes the way in which the phases are interconnected. The above mentioned results show that in all cured ternary epoxy/PVAc/PVPhBr blends, phase separated struc-

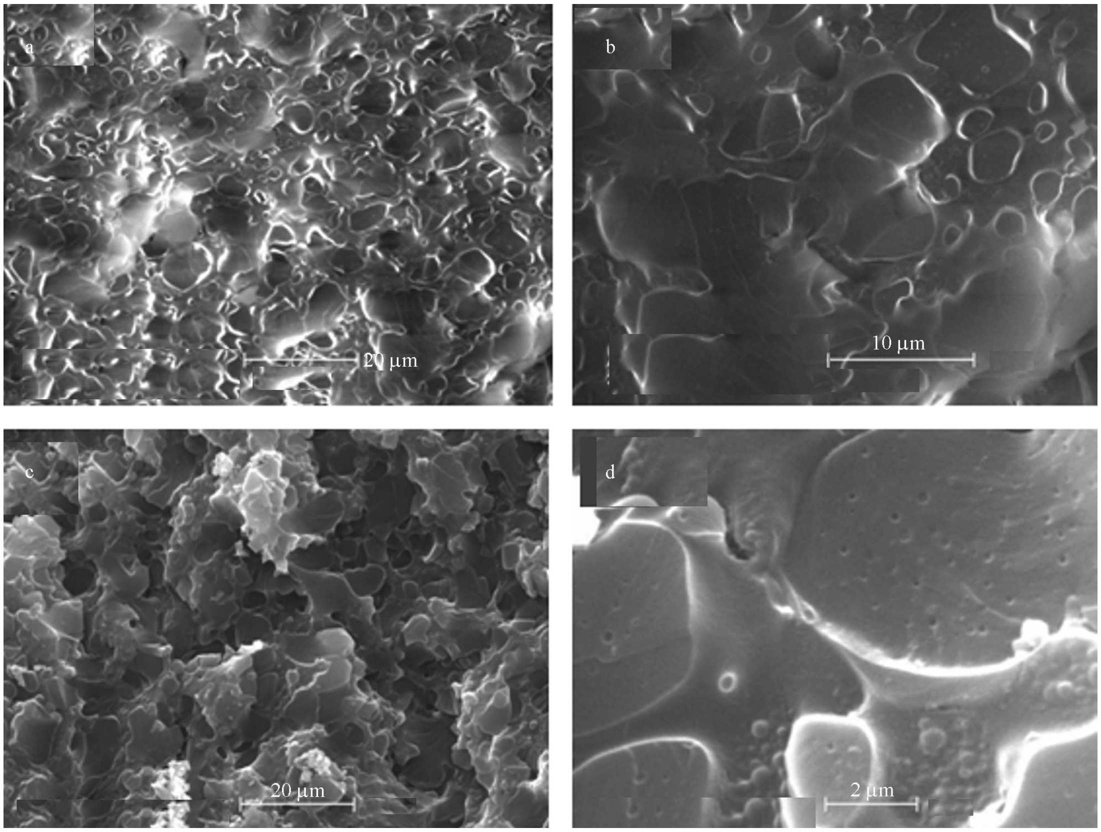

Fig. 7 ESEM micrographs of cured epoxy/PVAc/PVPhBr blends containing 10 mass% PVAc/10 mass% PVPhBr a – and b – without etching; c – and d – fracture surfaces etched with methanol

tures are generated and that the degree of separation of PVAc phase depends on the content of PVPhBr.

Conclusions

The curing of epoxy(DGEBA+DDM) is accelerated by the presence of PVPhBr which reacts with the epoxy. Cured binary epoxy/PVPhBr blends are transparent and do not present soluble fraction, they exhibit a single glass transition slightly lower than the one for neat epoxy and a unique phase is observed by ESEM. It can be concluded that epoxy/PVPhBr blends are homogeneous, forming a network, comprised of networking DGEBA/DDM and linear PVPhBr, of lower crosslinking density as PVPhBr content increases.

Cured ternary epoxy/PVAc/PVPhBr blends are opaque, and present two α-relaxations (T_g) indicating that they are phase separated into a PVAc rich phase and an epoxy network phase. For all the compositions studied the α-relaxation (T_g) of the PVAc rich phase appears at higher temperatures than the one in epoxy/PVAc blends. There is a correlation between the content of PVPhBr and the shift of α-relaxation (T_g) of the PVAc rich phase, which reflects an increasing content of PVPhBr in this phase, due to the hydrogen bonding between PVAc and PVPhBr. There is an increase of the height of E'' maxima associated to the PVAc phase relaxation as the PVAc content increases and it is a consequence of the change in morphology, which evolves from nodular to co-continuous. The presence of PVPhBr does not modify the critical composition, being the inversion located at 10 mass% of PVAc, but it changes the way in which the phases are interconnected. Therefore, in cured ternary epoxy/PVAc/PVPhBr blends, phase separated structures are generated and the degree of separation of PVAc phase depends on the content of PVPhBr.

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