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MORPHOLOGY AND DYNAMIC MECHANICAL PROPERTIES OF EPOXY/POLY(STYRENE-co-ALLYLALCOHOL) BLENDS
Influence of hardener nature

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Blends based on epoxy resins and a random copolymer, poly(styrene-co-allylalcohol) (PS-co-PA) were studied, analysing the effect of epoxy nature. The epoxy cross-linking reaction was carried out by homopolymerisation, using an imidazole as initiator, and by addition of several amine hardeners. The imidazole acts as initiator of anionic epoxy etherification and as catalyser of epoxy-hydroxyl reaction. Important differences were observed on the network structure and phase behaviour of blends depending on the nature of epoxy matrix. These cause that the blends present different morphologies and different dynamic mechanical properties.

Keywords: *epoxy blends, polyalcohol, polystyrene, TEM*

Introduction

The field of epoxy thermoset/thermoplastic (TP) blends has received considerable attention during the past decade [1–3]. The aim is to enhance the mechanical properties of epoxy resins with a dispersed TP rich phase. The presence of a secondary phase can cause an increase of the fracture toughness, through the crack deviation from its original plane, which implies that the energy required for the crack propagation increases [3]. However, little improvement was sometimes obtained due to the poor adhesion between phases. Recently, ternary blends consisting of two linear TP polymers and the epoxy resin are being studied [4–8]. The third component added usually is a copolymer with an epoxy-miscible monomer, enhancing its compatibility. Important toughness improvements have been reported on these materials regards to non-modified epoxy resin [4].

The phase behaviour and the morphology of ternary epoxy blends are much more complicated than those of binary blends [5, 7]. These systems can be separated on two or three phases. Also, the third component can be differently segregated on any phase. The study of the interrelationship among the phase behaviour, morphology, composition of blend and cross-linking degree is of great practical importance. It is well known that the final mechanical properties of these materials are strongly affected by the resulting morphology and extent of phase separation.

Pascault *et al*. [9] have observed very different morphologies on a secondary blend modifying the epoxy hardener used. They found that the hardener nature affects both the miscibility during polymerization reaction and the reaction rate.

In this contribution, a new ternary epoxy blend is investigated based on the use of poly(styrene-co-allylalcohol) (PS-co-PA) as modifier [10]. The polystyrene (PS) is a good candidate as epoxy modifier [11] and the presence of alcohol monomer must enhance the epoxy compatibility, modifying the blend morphology and therefore, its final properties. Two amine hardeners have been used as cross-linking agents, 4,4'-diaminodiphenylsulfone (DDS) and 4,4'-methylenedianiline (DDM). Also, an imidazole is used as initiator/catalyser of epoxy homopolymerisation reaction [12]. This compound can also catalyse the epoxy/hydroxyl reaction, enhancing the compatibility between the blends components.

Experimental

Materials and sample preparation

The epoxy monomer used was diglycidyl ether of bisphenol A (DGEBA), manufactured 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 epoxy cross-linking process was carried out by two different curing reactions: addition of a hardener and homopolymerisation. The used hardeners were two aromatic amines, DDS and DDM and 1-methylimidazole (1MI) was used as initiator of epoxy homopolymerisation. The TP copolymer added was PS-co-PA. The main characteristics of the compounds are listed in Table 1.

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Table 1 Characteristics of components used

	M_n/g mol^{-1}	M_{eq}/g eq^{-1}	Polymerization degree	Status	Supplier
DGEBA	344.8	178 g/epoxy	n=0.03	liquid (T_g*=–18°C)	Ciba
PS-co-PA	1600	61.2 g/OH	x=15.4, y=1	liquid (T_g*= 61°C)	Sigma Aldrich
DDS	248.3	62.1 g/NH	–	solid	Fluka
DDM	198.3	49.6 g eq^{-1} NH	–	solid	Fluka
1MI	82.1	–	–	liquid	Sigma Aldrich

*It was measured by DSC

The binary mixtures based on DGEBA and low TP amounts (≤40 mass%) were prepared by mixing at 140ºC. After about 30 min, the solutions became transparent, which indicated miscibility. The curing agent, amine hardener or imidazole, was then added at different temperatures depending on the cure temperature and it was mixed for 5 min. The resultant mixture was poured into a steel mould, where the curing treatment was applied. The hardener was always used at the stoichiometric ratio while the amount added of 1MI was 2 mass% regard to DGEBA mass. The curing treatment applied was 210ºC for 3 h for the epoxy blend cured with DDS and 150ºC for 1 h for the homopolymerised epoxy. The curing of DGEBA/DDM/PS-co-PA blends was made at 150ºC for 1 h, followed by a postcuring treatment of 180ºC for 30 min.

Measurements

Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Mettler mod. 821 apparatus, calibrated with indium. The thermal scan was from 30 to 250ºC, at 10ºC min^{-1} in nitrogen atmosphere.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical measurements were carried out on a DMA Q800 V7.1 analyser from TA Instruments on single cantilever mode. The frequency was 1 Hz and the heating rate was 2ºC min^{-1} from 30 to 250ºC. The samples used were parallelepipedic bars (1.5×12.5×35 mm^3).

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on an ATI Matson spectrometer, collecting 64 scans which wavenumber range is from 4000 to 400 cm^{-1}, at 2 cm^{-1} of resolution. Measurements were carried out with the potassium bromide pellets.

Solid state nuclear magnetic resonance (NMR)

^{13}C 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*. [13] ^{13}C chemical shifts were externally refered to tetramethylsilane.

Scanning electron microscopy (SEM)

The morphology of the blends was analysed by SEM, using an ESEM Phillips XL30. To investigate the phase structure, the specimens were broken after being cooled down at liquid nitrogen temperature. Most of the micrographs were taken on environmental mode, at 0.6–0.7 torr. For high resolution micrographs, the surfaces were coated with a thin gold layer of about 20 nm thick.

Transmission electron microscopy (TEM)

The study of interphase generated between the epoxy matrix and TP domains has been carried out by TEM (Phillips Tecnai 20). Samples were microtomed at room temperature using an ultramicrotome (Leica EMFCS) equipped with a diamond knife. The resulting ultrathin sections were deposited on copper grids and stained in the vapour of an aqueous solution of RuO_4.

Results and discussion

Miscibility of uncured DGEBA/PS-co-PA mixtures

The binary mixtures were transparent and no visual heterogeneity was observed. To confirm its homogeneity, DSC study of DGEBA/PS-co-PA mixtures was made. Only a single glass transition temperature (T_g) was observed over the whole composition range. All these observations indicate that the blends were homogenous before curing. However, a great difference is obtained between the experimental and theoretical values of T_g, which are plotted in Fig. 1. The theoretical T_g values of homogenous blend were calculated using Fox equation [14]:

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

where T_g is the glass transition of the blend, T_{g1} and T_{g2} are the T_g values of the pure components and w_1 and w_2 are their mass fractions.

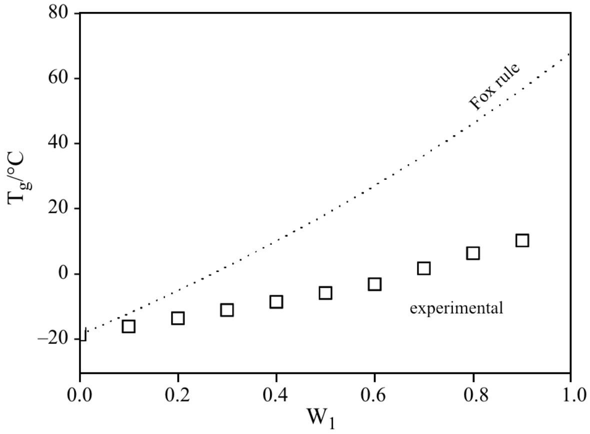

Fig. 1 Comparison of experimental T_g values with the predicted by Fox rule

The Fox rule determines the T_g values of 'ideal' miscible polymer blends. Miscible blends with strong interactions between components usually present positive deviations [15, 16]. The epoxy groups of DGEBA could interact through hydrogen bonds with the hydroxyl groups of PS-co-PA. The T_g – composition relationship obtained indicates that this interaction must be very weak. The important negative deviation of the experimental results must have other justification. This could be the breakage of the high self-association of PS-co-PA due to the hydrogen bonds of their hydroxyl groups. This fact would also justify the high T_g value of the pure copolymer, 68ºC, in spite of its low molar mass.

Phase behaviour and phase structure of cured blends

The dynamic mechanical thermal analysis provided information of both the viscoelastic properties and the morphology of blends. Figure 2 shows the dynamic mechanical properties of non-modified epoxy resins, cured with DDS, DDM and 1MI. As it was expected, all studied resins present only single α-relaxation, associated to the glass transition, indicating homogeneity. The maximum of tanδ for the epoxy resins cured with aromatic amine agents (DDS, DDM) is shifted at higher temperatures than ones obtained for the homopolymerised resin (1MI). It is known that the T_g value of homopolymerised epoxy resins is usually low, close to 80–120ºC [15, 16]. Comparing DDM and DDS, the higher α-transition temperature of resin cured with DDS is associated to its higher reactivity and the higher curing temperature applied [17]. The width of tanδ peak is indicative of sample homogeneity. The relaxation peak of homopolymerised resin is broad compared with those of epoxy-amine resins, indicating a large dispersion of relaxation times. This heterogeneity could be associated to the formation of areas with different cross-linking degree [18].

In contrast to the obtained α-transition temperatures, the average modulus (*E*') of the homopolymerised resin is higher than the epoxy resins cured with DDS and DDM, due to differences on network structure. DGEBA/1MI system is only constituted by DGEBA molecules linked by ether bonds, while the epoxy resins cured with amine agents are cross-linked by DDS or DDM molecules. The higher *E*' value of DGEBA/DDS than DGEBA/DDM is explained by its higher cross-linking degree confirmed by the higher α-transition temperature measured.

Figure 3 shows the tanδ *vs*. temperature plots of all studied blends cured with DDS, DDM and 1MI, and modified with different PS-co-PA contents. The presence of this copolymer causes different effects

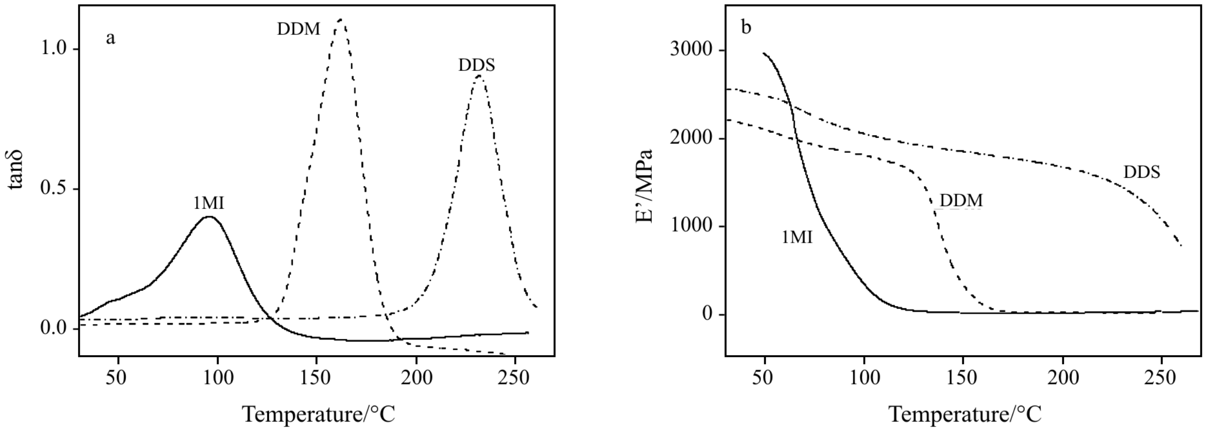

Fig. 2 Dynamic mechanical results: a – loss tangent (tanδ) and b – average modulus (*E*') *vs*. temperature for neat epoxy resins cured with DDS, DDM and 1MI

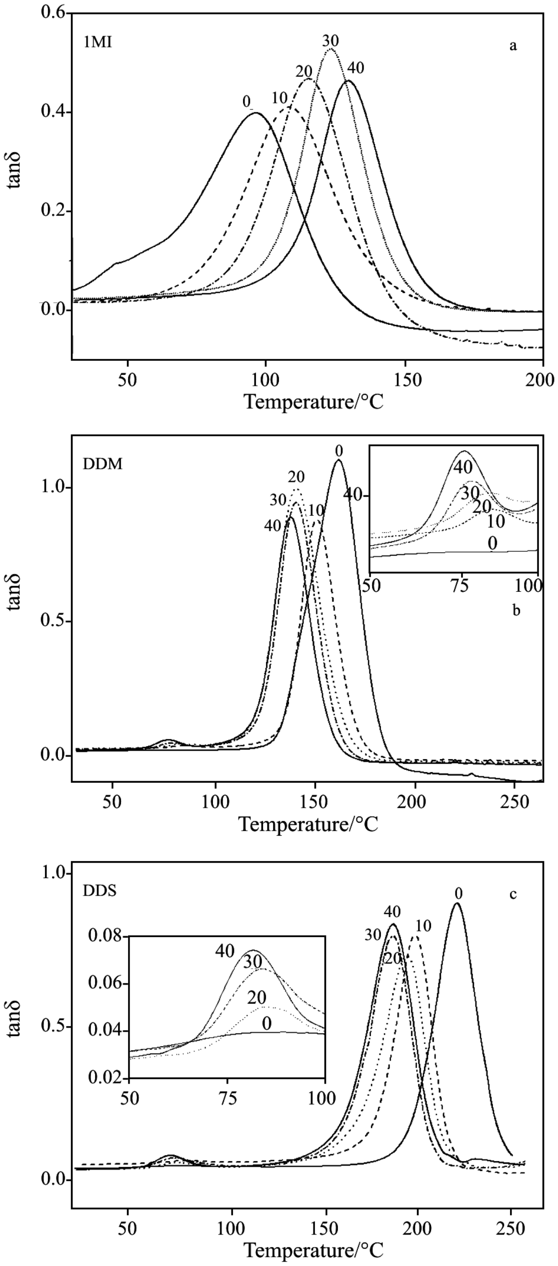

Fig. 3 Temperature dependence of tanδ of epoxy blends cured with a – 1MI, b – DDM and c – DDS and modified with different PS-co-PA contents (0, 10, 20, 30, 40 mass%)

depending on the nature of the epoxy resin. The epoxy/PS-co-PA blends cured with aromatic amine cross-linking agents, DDS and DDM, present two relaxation peaks. This behaviour implies phase separation. The maximum at higher temperature is associated to the epoxy rich phase while the smaller peak must be originated by TP rich phase. The presence of PS-co-PA also causes a proportional decrease of the α-transition temperature of epoxy resin. This fact implies a decrease of the epoxy cross-linking density, which can be justified by two reasons: one reason is the dilution effect, which means that the presence of TP on the system causes a decrease of epoxy conversion; on the other hand, the decrease of T_g may be also due to the incorporation of PS-co-PA into the epoxy resin. Posterior FTIR studies reveal that no free epoxy group was present in these blends, indicating a fully cross-linked system and rejecting the dilution effect.

Dynamic mechanical properties of the homopolymerised epoxy resin modified with PS-co-PA are radically different. Only single tanδ peak is measured for this system on all studied composition range, implying that it is homogeneous, without separated phases. This phase behaviour is justified because the used imidazole can act as initiator of epoxy homopolymerisation and as catalyser of epoxy/hydroxyl reaction [17]. The presence of one phase implies that the extension of this secondary reaction is high. This reaction also justifies the increase of α-relaxation temperature with the copolymer content added. The shift of tanδ peak at higher temperatures is accompanied with a decrease of its width. Therefore, the modification of homopolymerised epoxy resins with PS-co-PA gives as a result a more homogeneous resin with higher T_g values.

To study the chemical structure of the blends and to analyse the appearance of epoxy-hydroxyl reaction, the structure of epoxy network was studied by ^{13}C-NMR and FTIR. Figure 4 shows the spectra obtained by epoxy/PS-co-PA blends cured with DDS and 1MI. The spectra of DGEBA/DDM/PS-co-PA system are very similar to that of the blends cured with DDS. Not great differences are observed in function of PS-co-PA content, between the spectra of the blends cured with different amine aromatic agents, DDS and DDM. This happens as cause of the copolymer presents the same absorbance bands as the neat epoxy resins. The absence of the epoxy peak at 915 cm^{-1} indicates that the curing reaction reached high conversion and, therefore, there is scarcely dilution effect by the PS-co-PA introduction. The O–H stretching vibration (ν) was observed as a broad band at 3370 cm^{-1} on PS-co-PA spectrum and at 3480 cm^{-1} on neat epoxy resins. The TP spectrum presents a sharp band at 3570 cm^{-1}, which is also associated to O–H vibration. These observed differences are related to the OH interactions. The band at higher wavenumber is related to free hydroxyl groups (3650–3560 cm^{-1}) while the band of bonded OH is shifted at lower values (3550–3450 cm^{-1}). Also, the vibration of hydroxyl groups belonging to polymers usually appears at 3520–3200 cm^{-1}. This means that neat PS-co-PA contains hydroxyl groups, free and bonded through hydrogen bonds (self-autoassociation) and it seems that the content of free OH remains on the epoxy blends.

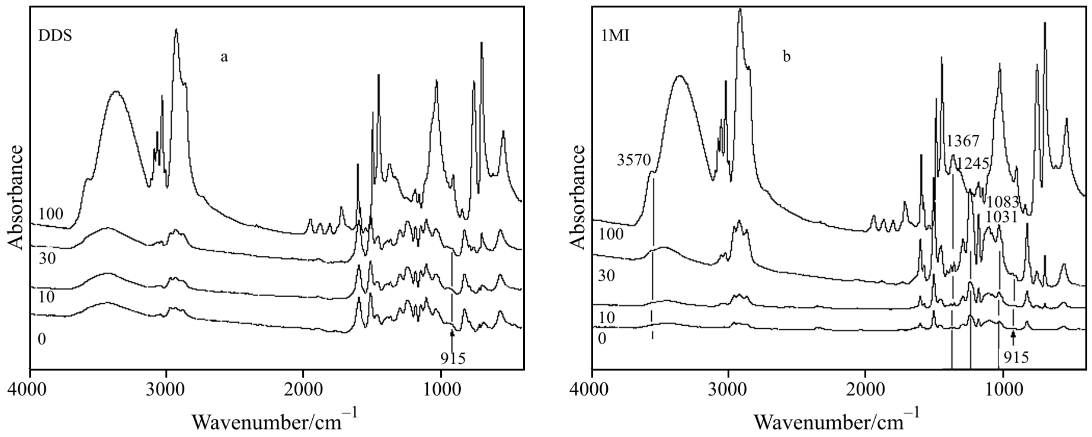

Fig. 4 FTIR spectra of cured neat resin (0%), the epoxy/ PS-co-PA blends modified with different copolymer content (10, 30 mass%) and of the pure PS-co-PA (100%) for a – DGEBA/DDS and b – DGEBA/1MI resins

More differences are observed on the spectra collected by the homopolymerised epoxy/PS-co-PA blends. In particular, the spectrum of pure PS-co-PA presents a band at 1367 cm^{-1}, associated to O–H bending out of plane vibration (δ_{oop}), which disappears on epoxy blends. Also, the relative intensity of the bands corresponding to symmetrical (1245 cm^{-1}) and asymmetrical stretching vibration of C–O–C bonds (1083 and 1031 cm^{-1}), widely increases with the PS-co-PA content. These observations confirm the chemical reaction between hydroxyl groups and epoxy rings formed by ether bonds on homopolymerised epoxy/PS-co-PA blends.

Only small differences were found between obtained ^{13}C-NMR spectra due to the high similarity of the chemical structure of the studied epoxy resins and the added copolymer. Figure 5 shows several spectra taken for neat epoxy resins cured with DDS, DDM and 1MI and for DGEBA/1MI/PS-co-PA blends with different TP contents. The main difference is the intensity of peak at 50 ppm, corresponding to oxirane ring. While this peak scarcely appears on the obtained spectra for the epoxy resins cured with aromatic amines, DDS and DDM, its intensity is relative important for the homopolymerised resin. This means that the epoxy conversion reached by DGEBA/1MI is lower and this justifies its lower glass transition temperature. However, the presence of PS-co-PA causes a proportional decrease of this peak until 30 mass%, where it disappears. This increase of the reached epoxy conversion is due to the epoxy-hydroxyl reaction. These results are in accordance with the increase of α-relaxation transition temperature of blends on DGEBA/1MI/PS-co-PA when the copolymer content increases.

Morphology of cured blends

Figure 6 shows several SEM micrographs of the studied epoxy/PS-co-PA blends. The micrographs were taken at different magnifications (2000×, 5000×, 25000× and 50000×) for a better observation of the samples morphology. According to the previous results, the homopolymerised epoxy/PS-co-PA blends are homogenous, without noticeable separated

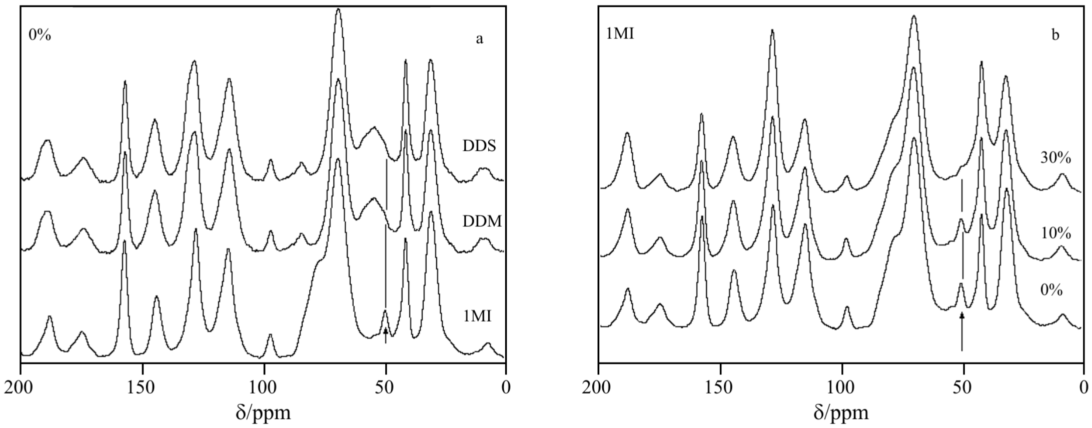

Fig. 5 ^{13}C-NMR spectra of a – cured epoxy resins (0%) and b – homopolymerised epoxy/PS-co-PA blends (1MI) with different PS-co-PA content

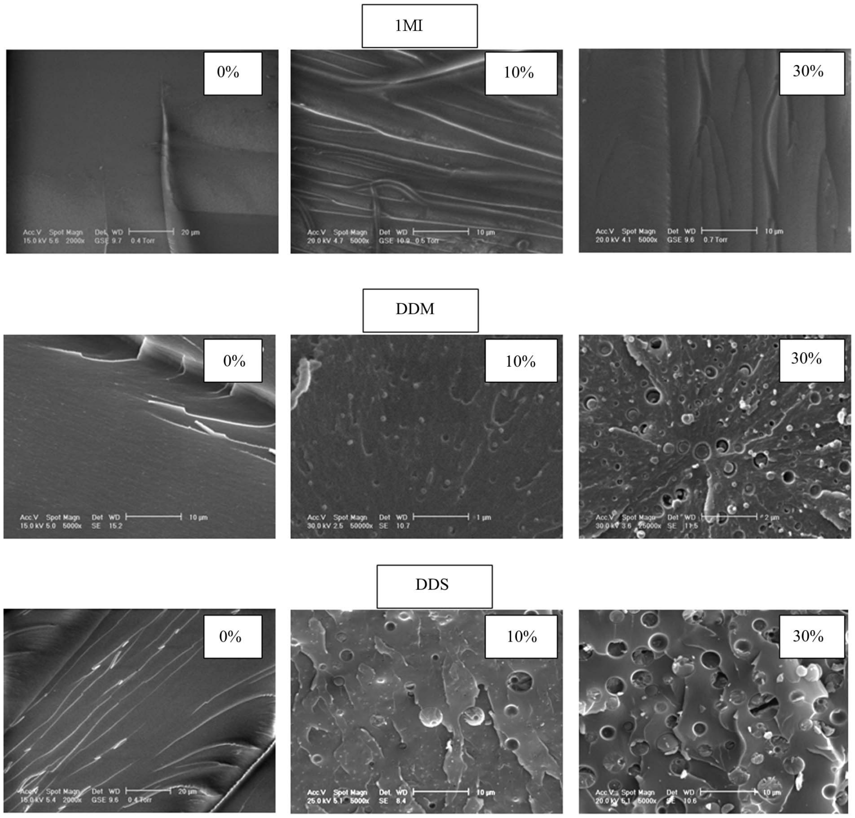

Fig. 6 SEM micrographs of epoxy/PS-co-PA blends with different copolymer contents (0, 10, 20 mass%) cured with 1MI, DDM and DDS, respectively

phases. In contrast, the blends cured with DDM and DDS show phase separation. This confirms that 1MI acts as initiator of epoxy homopolymerisation and as catalyser of epoxy-hydroxyl reaction.

The morphology observed on epoxy/PS-co-PA blends cured with DDS and DDM is heterogeneous. For all studied compositions (≤40 mass PS-co-PA), the blends are constituted by spherical rich TP domains dispersed by epoxy-rich matrix. The thermoset/TP blends present a critical composition value where the phase inversion occurs. From this composition, the blends are constituted by TP matrix with epoxy-rich domains. The value of this critical composition for DGEBA/PS-co-PA blends cured with DDS and DDM was calculated by Flory–Huggins model, obtaining 70 mass% for both systems. From the bibliography it can be deduced that the critical composition of most of studied epoxy/TP blends is usually close to 10–15 mass%. This great difference is due to the important differences on the molecular mass of the polymer modifiers. The copolymer used as modifier in this work only has 1600 g mol^{-1}. Both epoxy-amine/PS-co-PA blends present similar morphology, with separated phases, but the size of the PS-co-PA domains is radically different on each system. The average diameter of the blends domains is close to 240 nm and 2.3 μm for DDM and DDS hardeners, respectively. This important difference is justified because the phase separation mechanism which depends on numerous factors, such as the composition of blends, nature of curing agents and curing temperature. The studied blends are initially homogeneous and the phase separation occurs during the curing treatment due to the increase in molecular mass of the epoxy resin as a result of cross-linking. Therefore, this phenomena and the generated morphology are strongly dependent on the curing rate, which is very different for each studied resin.

A detail study of the final morphology of the phase separated blends was carried out by image analysis, using SEM afore software. Table 2 collects the obtained values of average domains diameter and particle density as function of PS-co-PA content. The particle density was calculated as number of domains per sam-

Table 2 Average diameter and density of domains of epoxy/PS-co-PA blends cured with DDS and DDM

TP/mass%	DDM		DDS	
	ϕ/nm	ρ/nm^{-2}	ϕ/μm	ρ/μm^{-2}
10	97±10	3.2	1.9±0.3	0.017
20	240±16	4.2	2.3±0.5	0.045
30	326±9	3.7	3.0±0.2	0.033
40	345±15	4.5	2.5±0.4	0.071

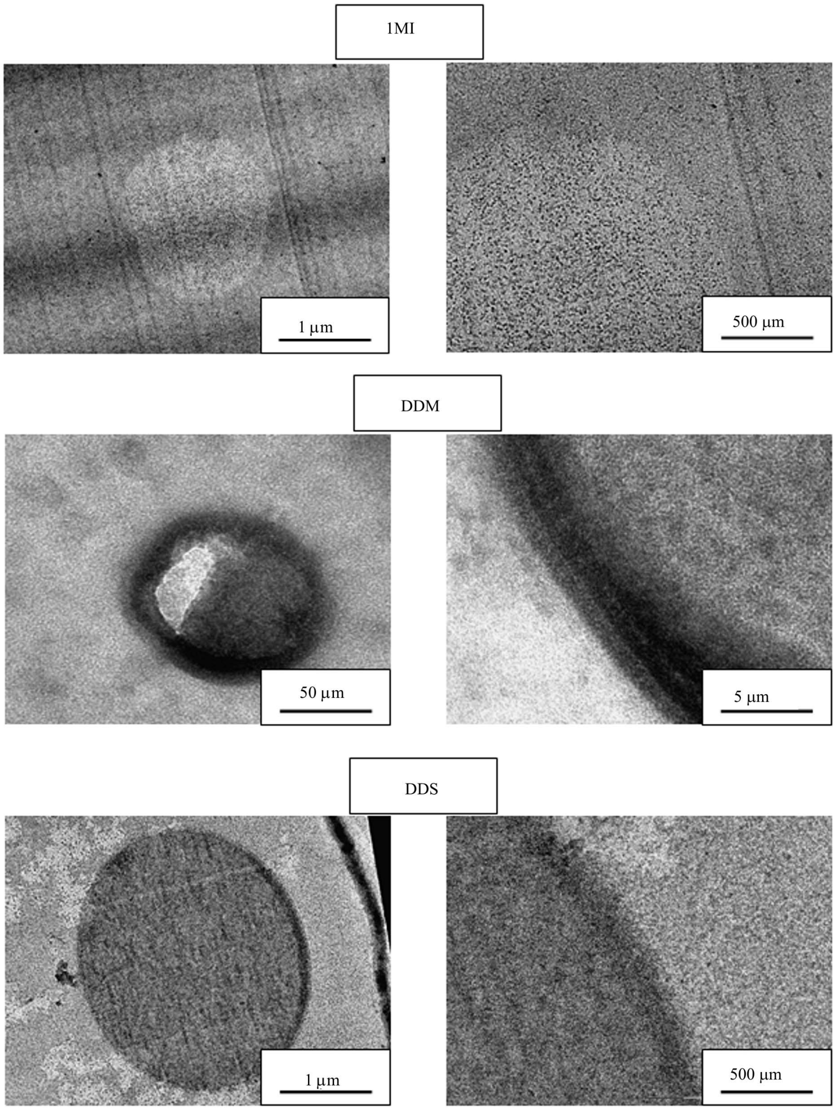

Fig. 7 TEM micrographs of epoxy/PS-co-PA blends with 10 mass% PS-co-PA and cured with 1MI, DDM and DDS, respectively

ple area. It is worthy to note that on DGEBA/DDM/PS-co-PA blends the average diameter of TP domains increases with the TP content while the density of these domains remains practically constant. In contrast, the blend cured with DDS presents different behaviour: the particle size remains basically constant and the density increases as the PS-co-PA content increases.

As well as phase separation morphology, the enhancement of the mechanical properties requires a good adhesion between phases. In the studied blends, the interfacial adhesion must be enhanced by the chemical reaction between epoxy rings of the matrix and hydroxyl groups of the PS-co-PA or H-bonding interactions between the two. The SEM micrographs showed no vacant spaces on the holes left by the removal of TP domains. Also, most of the TP domains are broken, indicating a strong interfacial adhesion. In order to analyse the interfacial region between the epoxy matrix and PS-co-PA domains, the samples were observed by TEM, after being dyed with RuO_4. Figure 7 collects the TEM micrographs obtained by epoxy resins modified with 10 mass% PS-co-PA. As it was expected, the resins cured with DDM and DDS present phase separation. However, despite of SEM micrographs, the TEM images of modified homopolymerised resin also shows heterogeneity. It can be observed spherical light marks, approximately 1.3 μm in diameter, on the dark matrix. However, the nature of the dispersed domains seems to be different. The blends cured with DDS and DDM present physically separated phases well defined with a clear interface area between the epoxy matrix and the PS-co-PA domains. The DGEBA/1MI/PS-co-PA system shows chemical heterogeneity, without clear physical separation. This difference justifies that the previously used techniques, such as DMTA or SEM, did not indicate the existence of heterogeneity.

On the other hand, at very high magnification, it is possible to study the interfacial region of blends. Both epoxy-amine/PS-co-PA blends present a clear interface, whose size is proportional to the domains size, close to 50 and 2 nm for the epoxy blend cured with DDS and DDM, respectively. The interfacial region is rightly bonded to the phases, matrix and domains. Unstitched areas were not observed, indicating a good adhesion between the epoxy matrix and PS-co-PA domains. The presence of the interface confirms the reaction between epoxy rings of resin and hydroxyl groups of copolymer.

Conclusions

The influence of epoxy hardener or catalyser on the network structure, phase behaviour and final morphology of PS-co-PA/epoxy blends has been studied. The blends formed by the homopolymerised epoxy network were radically different from those constituted by epoxy-amine matrix. The use of imidazole as initiator of anionic etherification reaction increased the miscibility between epoxy and PS-co-PA as this compound can also catalyse epoxy-hydroxyl reaction, forming homogeneous blends. These blends presented only one glass transition, which T_g increases with the PS-co-PA content. However, the micrographs at very high magnification, obtained by TEM, showed spherical heterogeneities, associated to compositional differences.

The epoxy blends obtained by epoxy-amine reaction were formed by an epoxy matrix with spherical PS-co-PA domains. Therefore, these blends presented two glass transitions, associated to each phase, epoxy and PS-co-PA. The main difference between the epoxy-amine/PS-co-PA blends cured with DDM and DDS was the thermoplastic domains size. The epoxy blends cured with DDM presented domains much smaller than those cured with DDS. It was observed by TEM a well-defined interfacial region. The absence of unstitched areas indicated a good adhesion between the epoxy matrix and PS-co-PA domains, due to the strong interactions between epoxy rings of resin and hydroxyl groups of copolymer.

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