Influence of the Network Structure and Void Content on Hygrothermal Stability of Resol Resin Modified with Epoxy–Amine

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ABSTRACT: Epoxy–amine was blended with two resol resins to study the influence of the final network and void content on the water absorption of these systems. To characterize the network structure of the blends, infrared analyses were performed. It was observed that a diminution in the crosslink density of the network and the reaction between the epoxy and resol have been occurred. From dynamic–mechanical analyses, a diminution in the T_g value and an increment in the height of the tan δ peak with the epoxy–amine content added to the resol were observed. Thermogravimetric analysis showed that the thermal stability of the resol was reduced by the addition of epoxy–amine as well as a lesser crosslink network for the blends with higher epoxy–amine content. The maximum water uptake and the diffusion coefficient were related with the chemical structure and void content of the specimens. On one hand, the maximum water uptake was observed to depend on the void content of the blends. On the other hand, the diffusion coefficient appears to be related with the local motions of the polymeric chains and with the hydrophilic character of the materials. This behavior was observed for the two resols studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 588–597, 2006

Key words: epoxy–phenolic; blends; morphology; viscoelastic properties; water absorption

INTRODUCTION

Phenolic resins are widely used commercially because of their excellent flame retardance and low cost, and there has also been much academic interest in understanding the mechanism of curing and decomposition of the phenolics.[1–12] However, phenolic resins during curing reactions produce volatile by-products such as water and formaldehyde, which lead to voids in the materials,[13] and because of their high crosslinking density it results in a brittle material. A lot of work was done to produce a tough resin based on phenolic resin,[14–17] and one way to do this is blending the phenolic with epoxy resin. Epoxy resins are used for applications where high strength and toughness are needed. In previous work,[18] we have studied epoxy–resol blends to be used as matrices for fiber reinforced composites. In that work, the processability and mechanical properties of the resol were improved by blending with epoxy. Several authors have proposed reactions that could occur between epoxy and phenolic resin[19–21] that involve on one hand the reaction of the hydroxyl group of the phenol with the epoxy group, and on the other hand the reaction between the methylol of the phenolic resin and the secondary hydroxyl of the epoxy. Also, a phenolic resin was used as a curing agent for epoxy where the epoxy is the major component[22,23] to take advantage of the flame retardant properties of phenolic resin.

The presence of water has a devastating effect on the thermomechanical properties of a resin and their composites.[24–26] The relationship between the water uptake and the corresponding structure–property relationships are of great practical interest and are useful to characterize the different polymers especially those largely used in composites.

The aim of the present work is to study the influence of the network structure and void content on the water absorption of the epoxy–amine–phenolic blends.

EXPERIMENTAL

Materials

Resol-type phenolic resins were prepared with a formaldehyde to phenol molar ratio (F/Ph) = 1.6 and 2.0 (R1.6 and R2.0) in the presence of a solution of 40% NaOH. The pH was kept at 9.0 and the mixture re-

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acted for 2 h at 90°C in a glass reactor with a low-velocity stirrer, thermometer, and reflux condenser. The mixture was neutralized with a solution of boric acid until a pH = 6.8–7.0 was attained. The dehydration of resol was performed inside the same reactor in a vacuum at 75–80°C until all the water was totally extracted. The resols were kept at −10°C after synthesis until the moment they were used.

The epoxy resin 1,4-butanedioldiglycidylether from Ciba Geigy ™ (epoxy equivalent = 114.9 g/equiv) was used and the aliphatic amine triethylenetetramine technical grade (TETA, 70%) was used as a curing agent. The equivalent weight was 34.5 g/equiv H. The epoxy–amine system was used in stoichiometric ratio.

The resol–epoxy–amine blends were prepared by mixing the resol with 10, 20, and 30% (w/w) of epoxy–amine.

To limit bubble formation, resols were gradually cured through increasing temperature steps of 3 h each: 40, 60, 80, 100, 130, 150°C, and 4 h at 180°C. The blends were cured using the following curing cycle: 2 nights at room temperature, 8 h at 80°C, and 6 h at 180°C.

Testing procedures

Dynamic–mechanical tests were performed in a Perkin–Elmer DMA-7 unit in a three-point bending mode with a fixed frequency of 1 Hz and a heating rate of 5°C/min. The specimens used for these tests were cut from plaques obtained by curing the resins between two pieces of glass previously treated with a silicone release agent from Siliar S.A., Argentina.

Fourier transform infrared (FTIR) spectra (drift mode) were acquired with a Mattson Genesis II spectrometer, with a spectral width of 600–4000 cm^{-1}, 32 accumulations, and a 2 cm^{-1} resolution. For comparison purposes, the spectra were normalized with the intensity of the band near 1600 cm^{-1}, which correspond to the stretching C═C of the benzene ring.[27]

The water absorption measurements were made by immersing the samples in a water bath at 80°C, and the weight changes with time were recorded. The samples were cut from plaques prepared as previously explained for the DMA tests. The dimensions of the samples were 50 mm × 7.5 mm × 2 mm.

Scanning electronic microscopy (SEM) was performed on the surfaces of the specimens to analyze their void content. Polished surfaces of the specimens were coated with a 300 Å gold layer and observed in a scanning electron microscope (JEOL JSM-6460LV).

The contact angle determination was made by the sessile drop method. Drops of ethylene glycol (Aldrich, 99.1%) and diiodomethane (Aldrich, 99%) were formed on the surfaces of plaques of the specimens. The contact angles made by the drops of these liquids were measured with a camera MV-50 (zoom 6×) and acquired with the software Image NIH. At least five drops per liquid were measured. To determine the total surface energy of the materials and their polar and dispersive components, the Owens and Went equation[28] was used:

$$0.5\gamma_2(1+\cos\theta) = (\gamma_1^d\gamma_2^d)^{1/2} + (\gamma_1^p\gamma_2^p)^{1/2} \quad (1)$$

where 1 and 2 refers to the solid and liquid, respectively; γ^d the dispersive component, and γ^p the polar component of the surface energy; and θ is the contact angle. If the contact angles made by two liquids of known γ^d and γ^p are measured, it is possible to solve the eq. (1) and infer the $\gamma_1{}^d$ and $\gamma_1{}^p$ for the material. Then, the total surface energy is estimated from eq. (2):

$$\gamma_1 = \gamma_1^d + \gamma_1^p \quad (2)$$

The surface energy components of probe liquids used for the contact angle measurements are listed in Table I.

TABLE I
Surface Energy Components of Probe Liquids for Contact Angle Measurements[29]

	Total surface energy (γ) (mN/m)	Dispersive component (γ^d) (mN/m)	Polar component (γ^p) (mN/m)
Ethylene glycol	47.7	30.1	17.6
Diiodomethane	50.8	48.5	2.3

RESULTS AND DISCUSSIONS

To study the viscoelastic behavior of the epoxy–amine–resol blends dynamic–mechanical analysis were performed. The tan δ curve for the series of the resol 1.6 and 2.0 and different percentages of epoxy–amine are shown in Figures 1 and 2, respectively. A big transition was observed close to 230–280°C, and there appears another peak as a shoulder close to 80°C. The mixture of resol and epoxy–amine could be thought of as a heterogeneous system with two regions: one with a higher content of epoxy, and the other region with a higher content of resol, but this hypothesis cannot be taken into account because the net resol also has the two transitions mentioned previously. As a consequence, the presence of these two transitions could be due to two different movements on the network: the shoulder could be a secondary relaxation due to rotational movements of pendant chains, or oscillations of aromatic rings around the chain axis.[30] Figure 3 shows the glass transition temperature (T_g) of the blends, determined as the maximum of the tan δ peak, and the height of tan δ peak for each resol series. It was observed that the T_g value

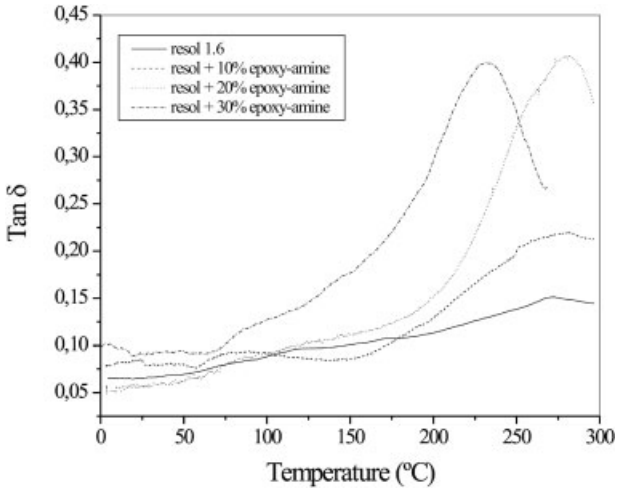

Figure 1 tan δ curves from DMA analysis of the resol with F/Ph = 1.6 and their blends with epoxy–amine.

decreases with the increment of the epoxy–amine content in the blends. Additionally, the height of the tan δ peak that is related with the damping of the polymeric chains increases when up to 20% of epoxy–amine is added to the resol. This should indicate that the addition of epoxy–amine to the resol produces a more flexible and lesser croslink network. The resol resin has a network with a high crosslink density and an important quantity of aromatic rings, which produces a high T_g value. Inversely, the epoxy–amine system used has a low T_g value because both the epoxy resin and the amine have an aliphatic structure providing the flexibility to the network of the blends. The T_g value of the epoxy–amine system was 1°C determined by the DMA.

Different equations have been developed to predict the glass transition temperature behavior of polymer

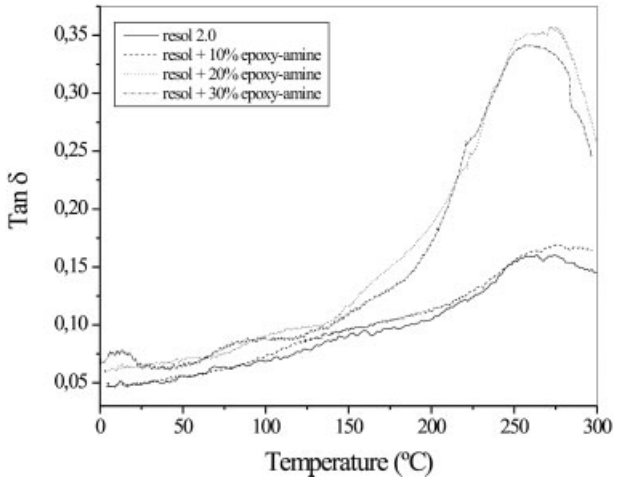

Figure 2 tan δ curves from DMA analysis of the resol with F/Ph = 2.0 and their blends with epoxy–amine.

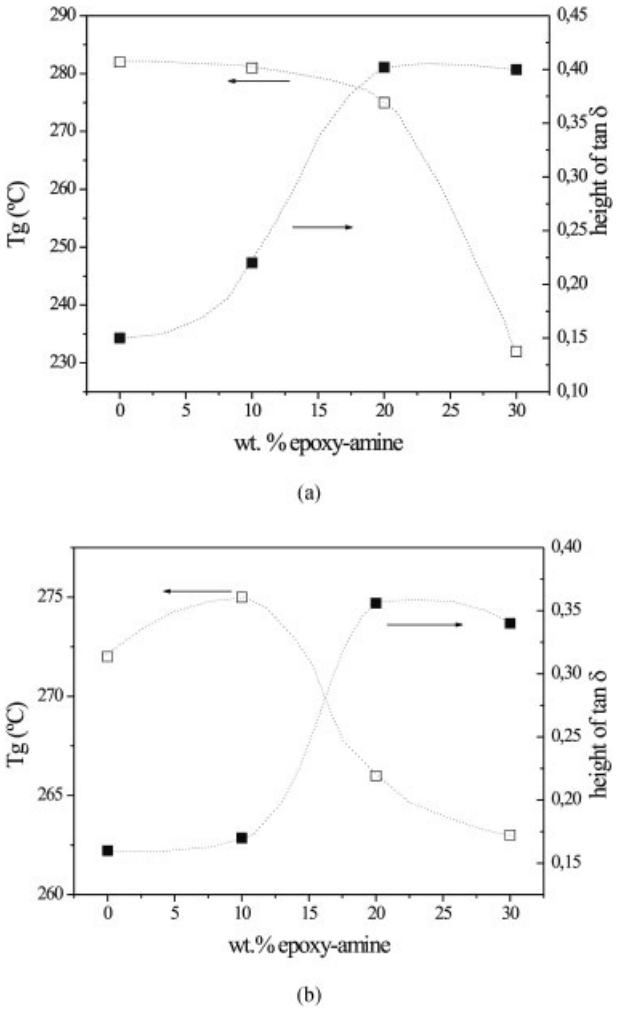

Figure 3 Glass transition temperature and height of tan δ peak for the epoxy–amine blends of resol with F/Ph = (a) 1.6 and (b) 2.0.

blends but the Kwei equation[31] is applicable when there are specific interactions in the blend, as in the system used in this work. The T_g of the blend expressed by the Kwei equation is as follows:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \qquad (3)$$

where w_1 and w_2 are the weight fractions, T_{g1} and T_{g2} represent the glass transition temperatures of the components, and k and q are the fitting constants. The parameter q is a measure of the strength of the hydrogen bond in the blend. The experimental T_g values of the blends were introduced into this equation and the k and q parameters were fitted (Fig. 4). The resulting q values were 225 and 318 for the resol 1.6 and 2.0, respectively, reflecting a stronger intermolecular interaction between the epoxy–amine and the resol 2.0. Moreover, this indicates that the resol 2.0 has a higher quantity of free OH groups capable to form hydrogen

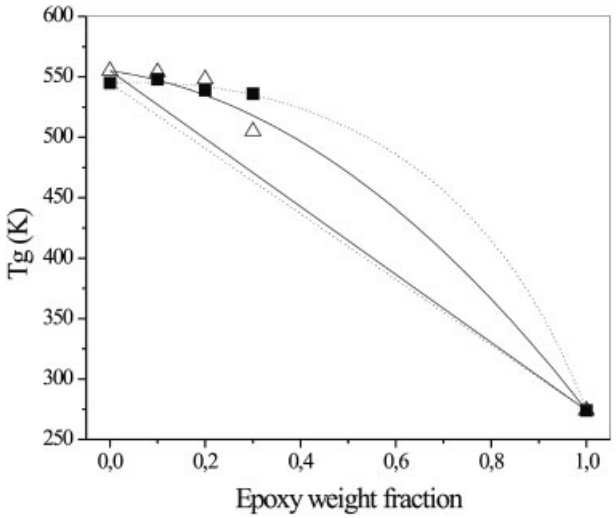

Figure 4 T_g as a function of the blend composition with Resol 1.6: experimental data (Δ) and Kwei equation (−); and Resol 2.0: experimental data (■) and Kwei equation (. . . .).

bonds than the resol 1.6. This is in accordance with other previous work[12] where we found that the crosslink density of the resol 1.6 was higher than that of the resol 2.0, indicating that the methylol groups of the resol 1.6 have reacted forming methylene bridges in a higher extent than in the resol 2.0.

Subsequently, we have investigated the morphology of the epoxy–amine–resol blends through FTIR analysis. The spectra obtained for the resol 2.0 and their blends with epoxy–amine in the range 1620–850 cm^{-1} are shown in Figure 5. As it was described previously, reactions between phenolic and epoxy resin can occur including not only reactions between the phenolic hydroxyl and the epoxy group, to form a secondary hydroxyl and an ether group, but also further reaction between the phenolic methylol groups and the secondary hydroxyl groups of the epoxy to form an ether linkage.[10,19] Taking into account the products of the reactions mentioned earlier, an increment in the ether groups content will follow the addition of resol to the epoxy resin, while the content of epoxy ring, hydroxyls of the phenols, and methylols of the resols should decrease accordingly. The secondary hydroxyls of the epoxy are consumed and produced during the reactions so that they cannot be used to study the reaction. It was observed in Figure 5 that the characteristic bands of the ether groups, 1110 cm^{-1} [ν (COC)] and 1040 cm^{-1} [ν (φOC)] (where φ is the benzene ring),[27,32] became higher with the addition of epoxy–amine to the resol, indicating that the reaction between the epoxy and the resol has occurred. In addition, the band at 1211 cm^{-1} that correspond to the [ν (CO)] of the phenol shows a decrease with the epoxy–amine content in the blends. The band characteristic of the —OH of the phenol appears at 1365 cm^{-1}, but it is overlapped with the band that correspond to the —CH_3— groups of the epoxy, and so their variation cannot be taken into account because of these opposite effects. Equally the band at 915 cm^{-1} [32] that correspond to the epoxy ring is overlapped with the band of the δ (φ-H) of the substituted benzene ring of the phenolic resin, and so it cannot be used to study the reactions. On the other hand, the bands at 1475 and 1445 cm^{-1} [27] correspond to the ortho–para′ and ortho–ortho′ methylene bridges that are formed during the curing reaction of the resol. It was observed in the spectra (Fig. 5) that this bands decrease with the epoxy–amine content in the blends. This result indicates that the addition of epoxy–amine to the resol form a lesser crosslink network, in accordance with the results obtained by DMA. The spectra of the resol 1.6 and their blends showed similar results.

Another way to characterize the structure of the blends is studying their thermal degradation. Themogravimetric analyses were done on each specimen and the curves of weight loss for the blends of resol 1.6 and 2.0 are shown in Figures 6 and 7, respectively. It was observed that the addition of epoxy–amine to the resol reduces their thermal stability. The beginning of weight loss is shifted to lower temperatures with the increment of the epoxy–amine percentage in the blends. In addition, the rate of weight loss at ~400°C also increases for the blends with higher epoxy–amine content. The degradation of methylene bridges occurs in this region, and we have found in previous work[33] that the rate of weight loss was faster for the lesser crosslink resols at 400°C. So, the addition of epoxy–amine to the resol should decrease the crosslink density of the network. On the other hand, the char residue at the end of the test diminishes with the epoxy–

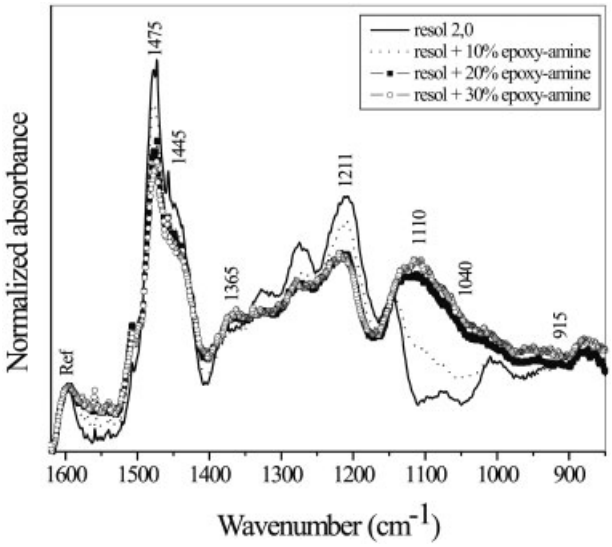

Figure 5 FTIR spectra of the Resol 2.0 and their epoxy–amine blends in the range 1650–850 cm^{-1}.

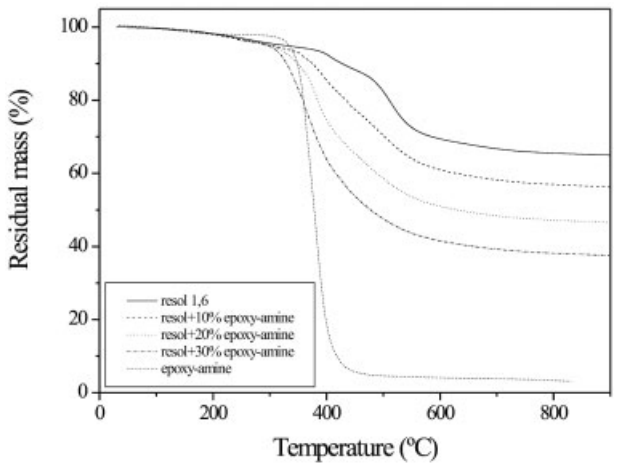

Figure 6 Percentage of residual mass versus temperature for the Resol 1.6 with different content of epoxy–amine.

amine content, thus reducing the insulating properties of the resol.

The absorption of water of the blends was measured and compared with that of the resol. Percent weight change or water uptake was calculated from

$$M\% = \frac{M_t - M_0}{M_0} 100 \tag{4}$$

where M_0 is the dry initial weight, and M_t is the weight of the specimen at each time. The weight changes of resols and its blends are shown in Figures 8 and 9.

Fick's second law of diffusion has been widely used to describe the uptake of moisture of several materials. Fick's law is applicable for homogeneous materials, and when no chemical interaction occurs between the absorbed water and materials. The material studied is

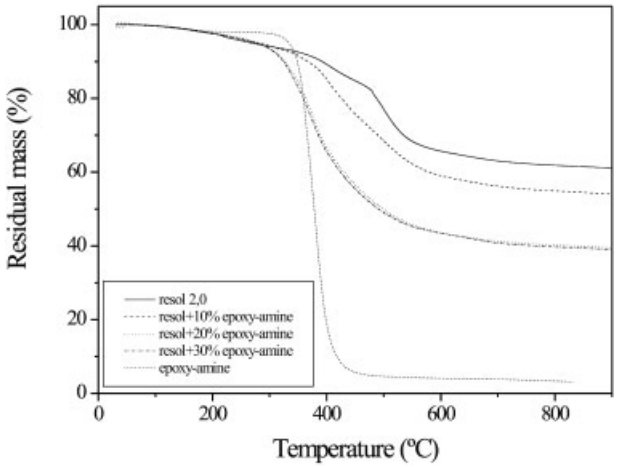

Figure 7 Percentage of residual mass versus temperature for the Resol 2.0 with different content of epoxy–amine.

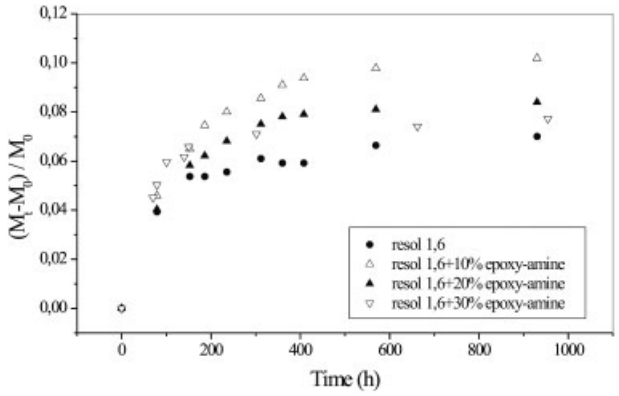

Figure 8 Absorbed water content in function of time for the Resol 1.6 and their blends with epoxy–amine.

not homogenous because of the voids and the chemical interaction between the water and the hydrophilic ends of the molecular chains that could occur. However, to compare the samples between them, an effective diffusion coefficient (D_x) was considered here. The eq. (5) proposed by Crank[34] was used as a simplified solution of the Fick's law for the thin plate geometrical system

$$\frac{M_t - M_0}{M_\infty - M_0} = 1 - \frac{8}{\pi^2} \sum_{n-0}^{x} \frac{\exp(-(2n+1)^2 \pi^2 (D_x t/h^2))}{(2n+1)^2} \tag{5}$$

where D_x is the effective diffusion coefficient, t is the immersion time, M_∞ is the maximum relative water uptake value in each case, and h is the thickness of the specimen. It is necessary to remark that these values are not equilibrium values, because extraction of the

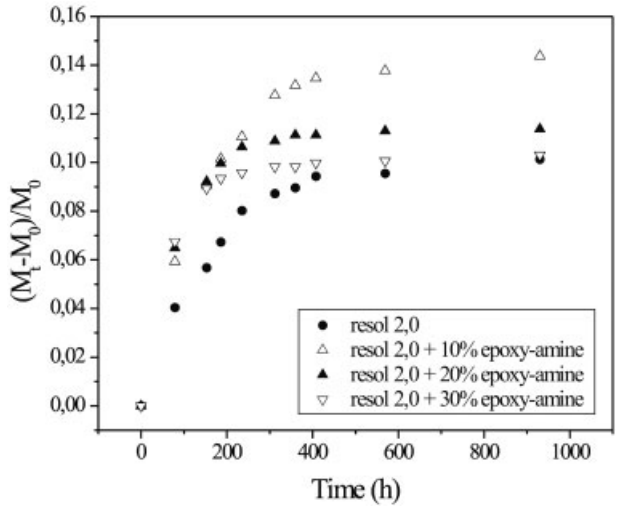

Figure 9 Absorbed water content in function of time for the Resol 2.0 and their blends with epoxy–amine.

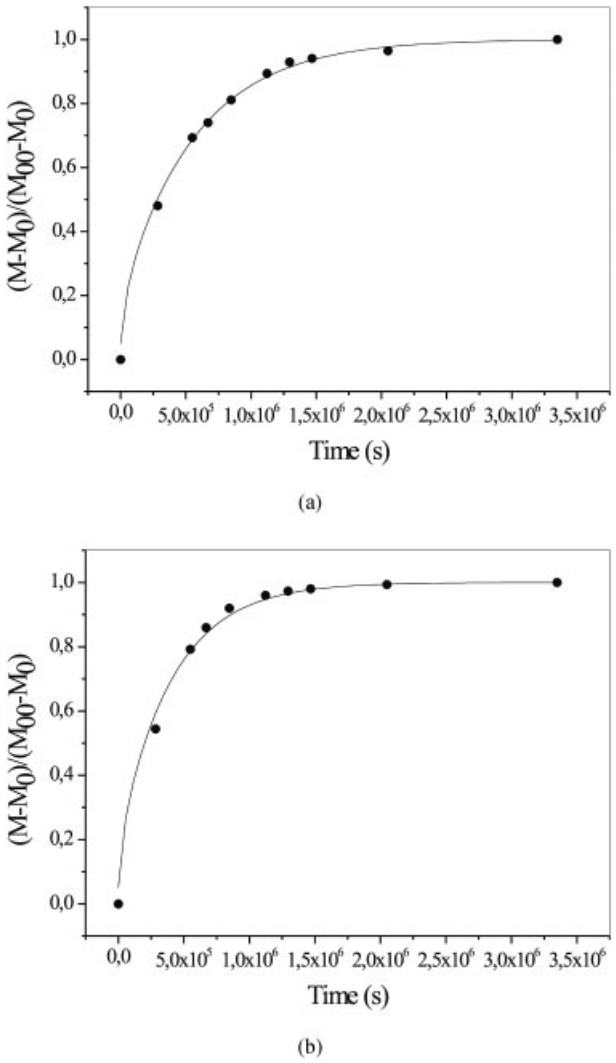

Figure 10 Fitted experimental values for the blends with 20% of epoxy–amine and the resol with F/Ph = (a) 1.6 and (b) 2.0.

soluble occurs at the same time. The D_x coefficient was estimated by this equation fitting the experimental values obtained for each specimen by means of the fitting method of Marquard under the Origin 6.0 version using a seed value. As an example, Figures 10(a) and 10(b) show the fitted experimental values with the model expression of eq. (5) for the blends of each resol with 20% of epoxy–amine. Experimental data are in good agreement with model prediction for all the systems analyzed. Figure 11 shows the diffusion coefficient obtained for the blends with the two resols studied. It was observed that the diffusion coefficient increases with the epoxy–amine content in the blends. On the other hand, the maximum relative water uptake (M_∞) has a maximum value for the blends with an epoxy–amine content of 10 wt %, as shown in Figure 12.

Certain authors have found that the absorption of water of polymers is directly related with their free

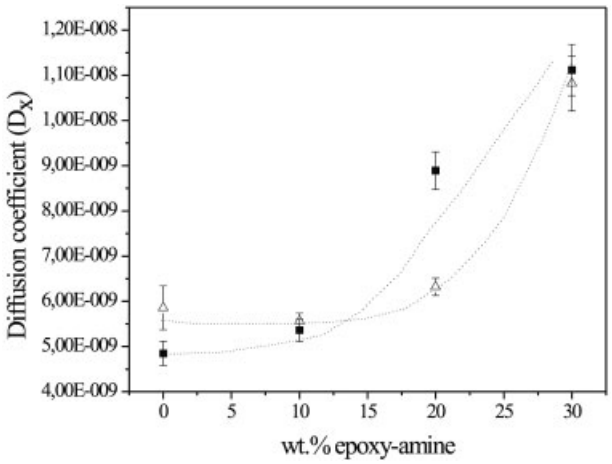

Figure 11 Diffusion coefficient values for resol of F/Ph molar ratio of 1.6 (Δ) and 2.0 (■) in function of the epoxy–amine content.

volume fraction while others have found that it is linked to the presence of polar groups capable to form hydrogen bonds with water molecules.[35] Other authors[36–38] have proposed different modes of water absorption that involve since the water that fills the microcavities of the network to water molecules trapped in the crosslinks network of the matrix. Merdas et al.[35] also have found that there is apparently no influence of the large-scale structure (crosslinking) of the polymer on water absorption of vinylester-epoxy resins.

To relate the water absorption with the microstructure of the blends, a SEM micrograph was performed on each sample (Figs. 13 and 14). The micrographs showed the presence of voids in all of the specimens analyzed, but a change in the quantity, size, and pattern of these voids was observed. The samples with low epoxy–amine content had only spherical voids

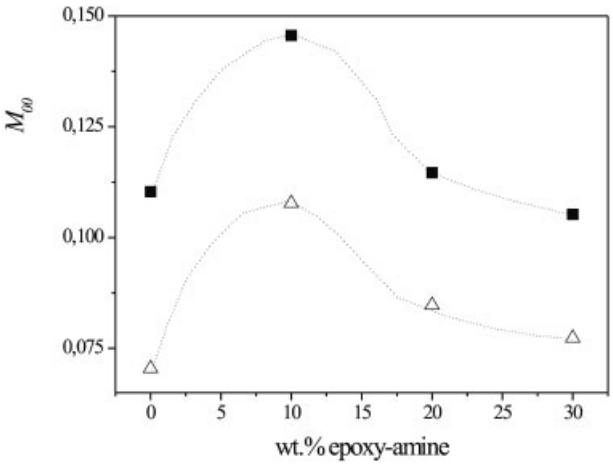

Figure 12 Value of M_∞ for resol 1.6 (Δ) and 2.0 (■) and their mixtures with epoxy–amine.

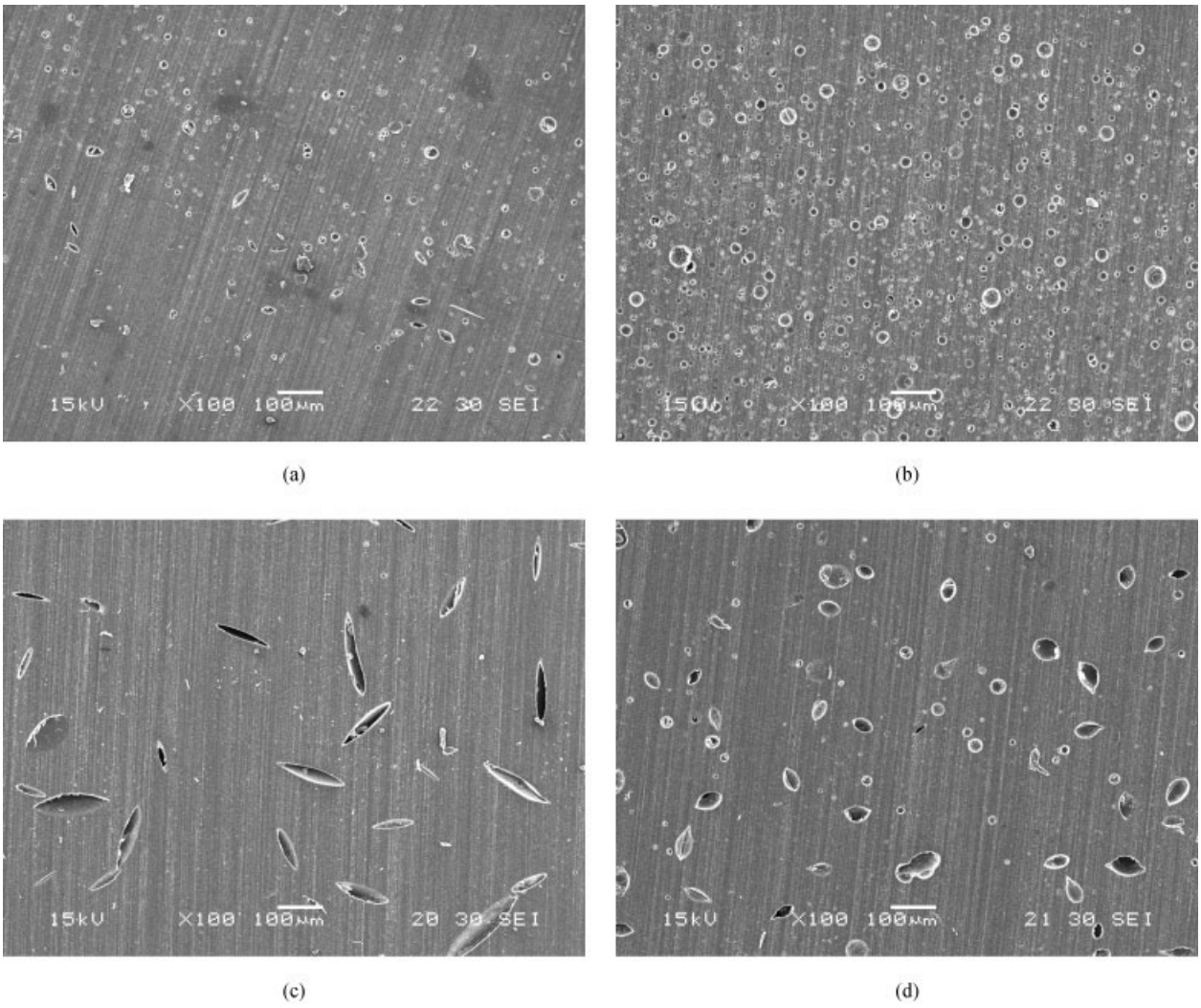

Figure 13 SEM micrographs for a resol with F/Ph = 1.6 (a) and their mixture with 10 wt% (b), 20 wt % (c), and 30 wt % (d) of epoxy–amine.

and the other samples with epoxy–amine content higher than 10 wt % presented longitudinal cracks. The spherical voids can be due to the evaporation of water and formaldehyde during the resol crosslinking reactions, because the condensation reaction produces water and formaldehyde as previously studied.[14] The longitudinal cracking can be formed during the reaction between the epoxy and resol; because of the low T_g value of the network, the spherical voids can be compressed and there appears the kind of cracks similar to the fracture behavior of a glass material. The void content in the specimens was measured from the SEM micrographs and the results are shown in Figure 15. Comparing Figures 12 and 15 it was observed that the void content vary in a similar way than M_∞ with the epoxy–amine content in the blends. So, the void content seems to be one of the factors that largely influence the maximum relative water uptake.

It was reported that in glassy polymers the local motions can play a crucial role in diffusion.[39] The local motion of a polymeric chain can be related to the amplitude of the tan δ curve, as was mentioned previously. Some differences arose in the height of the tan δ curves of the blends at 80°C, the temperature at which the water absorption tests were made. On one hand, the height of the tan δ curve of the resol 1.6 and their blends at that temperature (Fig. 1) showed a higher value for the blend with 30% of epoxy–amine compared with the others two blends and the resol, which values were quite similar. On the other hand, the same analysis for the resol 2.0 (Fig. 2) showed a higher height of tan δ curve for the blends with 20 and 30% of epoxy–amine than for the resol and the blend with 10% of epoxy–amine. Also, the heights of the last two were quite similar between them. Comparing this behavior with the diffusion coefficients obtained for each resol series (Fig. 11) it was possible to relate both results. The D_x and the local motions of the polymeric chains increase with the epoxy–amine content in the blends.

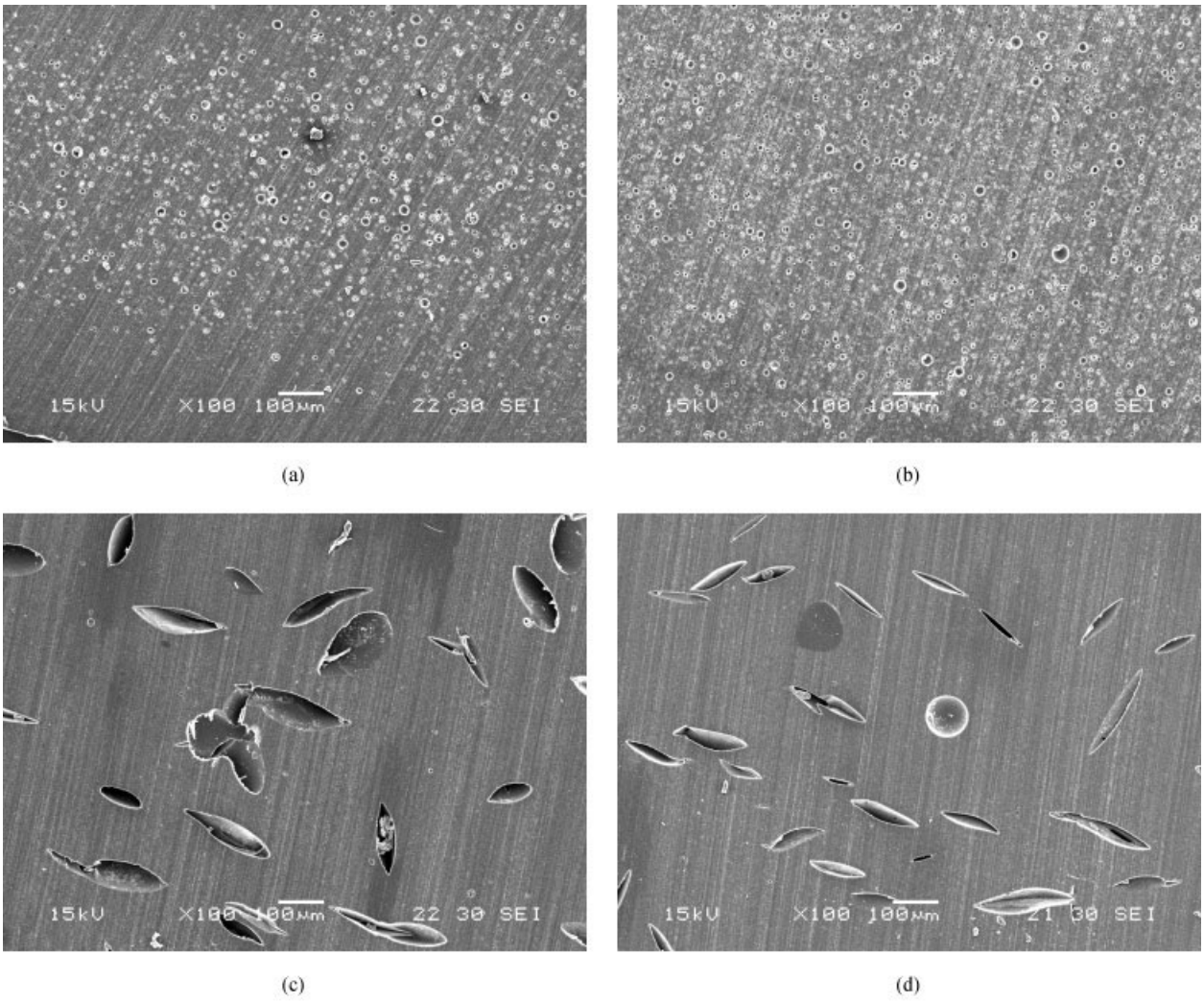

Figure 14 SEM micrographs for a resol with F/Ph = 2.0 (a) and their mixture with 10 wt % (b), 20 wt % (c), and 30 wt % (d) of epoxy–amine.

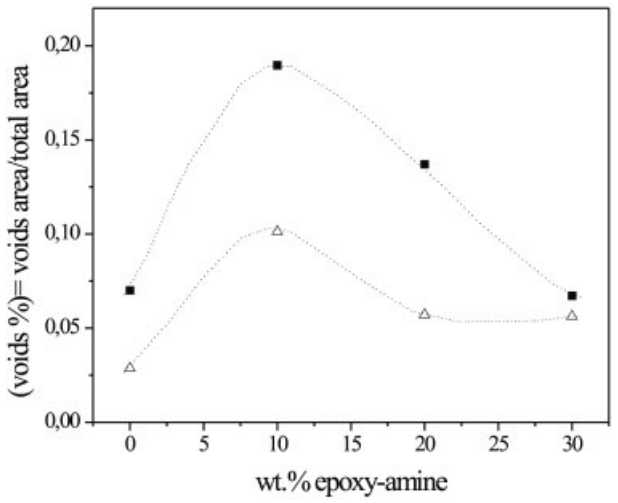

Figure 15 Percentage of voids for resol with F/Ph = 1.6 (Δ) and 2.0 (■) and their mixtures with epoxy–amine.

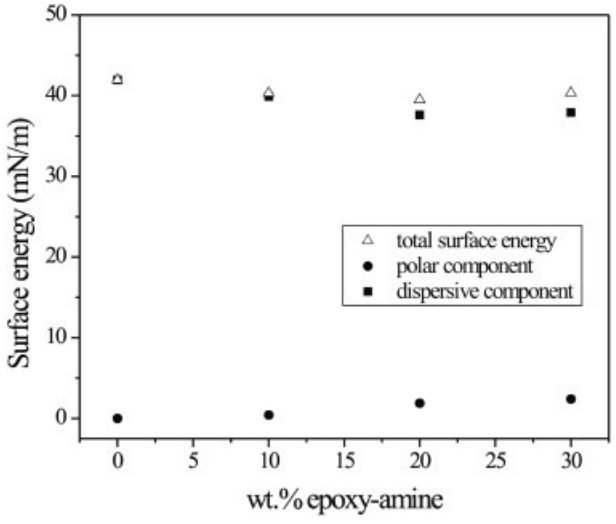

Figure 16 Surface tension and its components in function of the epoxy–amine content in the blend with resol of F/Ph = 1.6.

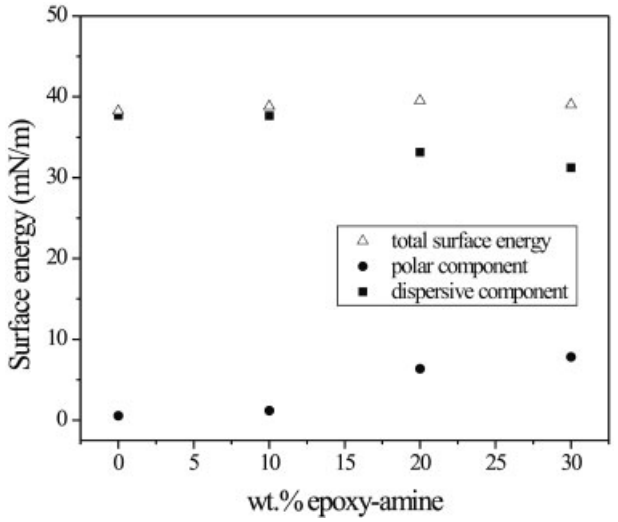

Figure 17 Surface tension and its components in function of the epoxy–amine content in the blend with resol of F/Ph = 2.0.

Additionally, the hydrophilic character of the blends was compared measuring the surface energy by means of the contact angle method. The polar and dispersive components of the surface energy calculated by means of the Owens and Went equation[28] are shown in Figures 16 and 17 for the blends of the resol 1.6 and 2.0, respectively. A diminution of the dispersive component was observed, as well as an increment in the polar component of the surface energy with the addition of epoxy–amine to the system. In spite of the slightly increment of the polar component of the surface energy it seems to vary following a similar behavior than the diffusion coefficient. Then, the variation in the hydrophilic character should be another factor that influence the D_x but in a minor proportion.

CONCLUSIONS

Blends of resol and epoxy–amine system were formulated and characterized. Two resols with different formaldehyde/phenol molar ratio were studied. From the analysis of the chemical structure of the blends, it was found that the epoxy reacts with the resol. A diminution in the crosslink density of the network with the addition of epoxy–amine to the resol was observed. There was found a diminution in the T_g and an increment in the height of the tan δ peak as well as a higher thermal degradation with the increment of epoxy–amine content in the blends. The diffusion coefficient and the maximum water uptake were related with the morphology of the specimens. The maximum water uptake depends principally on the void content of the blends and the diffusion coefficient appears to be related with the local motions of the polymeric chains and to the hydrophilic character of the materials. The behavior is not dependent on the formaldehyde/phenol molar ratio of the resol.

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