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Phase separation in polysulfone-modified epoxy mixtures. Relationships between curing conditions, morphology and ultimate behavior

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Abstract

Chemorheology of curing as well as the phase separation behavior of polysulfone (PSU)-modified diaminodiphenylmethane-cured diglycidylether of bisphenol-A epoxy mixtures have been studied using several techniques. The delay in polymerization for the modified mixtures with respect to that of the neat epoxy can be explained by dilution and viscosity effects. The immiscibility of these mixtures has been proved for various PSU contents and as a function of the precuring conditions used as well. The control of the generated morphologies can be performed only by varying the processing temperature. The thermal and dynamic viscoelastic behavior of the modified matrices has been examined and compared to the parent epoxy matrix. Finally, the mechanical properties, including fracture toughness, have been discussed in terms of the morphological behavior for an epoxy matrix modified with various amounts of PSU and for a 15 wt.% PSU-containing matrix precured at different temperatures. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy-polysulfone mixtures; Phase separation; Precuring

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1. Introduction

Nowadays, it is well recognized that phase separation is a necessary condition for improving fracture toughness in thermoplastic-modified thermosetting matrices [1–12]. Nevertheless, few investigations have been focused on the influence of the miscibility level in the final properties of mixtures containing the same components. For a determined thermoplastic-modified thermosetting matrix, two main factors control the final morphology of the mixtures: thermodynamics and the kinetics of phase separation during curing. Both can be modified by changing the thermoplastic content in the mixture and/or by varying the cure conditions [13–16].

Some controversies exist about the phase separation behavior of polysulfone-modified epoxy resins based in diglycidyl ether of bisphenol-A, DGEBA, and 4,4′-diamino-diphenyl methane, DDM. Thus, in the same way as McGrath et al. [17–20] who used other amines as curing agents, Moller et al. [21] have shown with model compounds the demixing behavior, and the several morphologies that can be obtained for mixtures polymerized with the DDM containing different amounts of polysulfone (PSU), precured at 120 or 150°C. On the contrary, Zhu et al. [22] have recently stated the existence of a single phase for the DDM cured epoxy mixtures containing a 15 wt.% of PSU, or less.

In this work, the influence of a thermoplastic content and that of a precure temperature for a prefixed amount of modifier in the generated morphologies and consequently, in the final properties of a DGEBA/DDM stoichiometric epoxy matrix modified with PSU has been investigated.

2. Experimental

The epoxy resin used was DER-332, a DGEBA kindly supplied by Dow Chemical, having an epoxy equivalent (EE) of around 175 and a hydroxyl/epoxy ratio close to 0.03. The curing agent was DDM (HT-972, kindly supplied by Ciba–Geigy). The thermoplastic was a PSU of bisphenol-A, PSU, Udel P-1700, provided by Amoco Chemical, with a $M_n = 38\ 000$ and a $M_w = 63\ 000$, as measured by gel permeation chromatography in a Waters 150-C ALC/GPC

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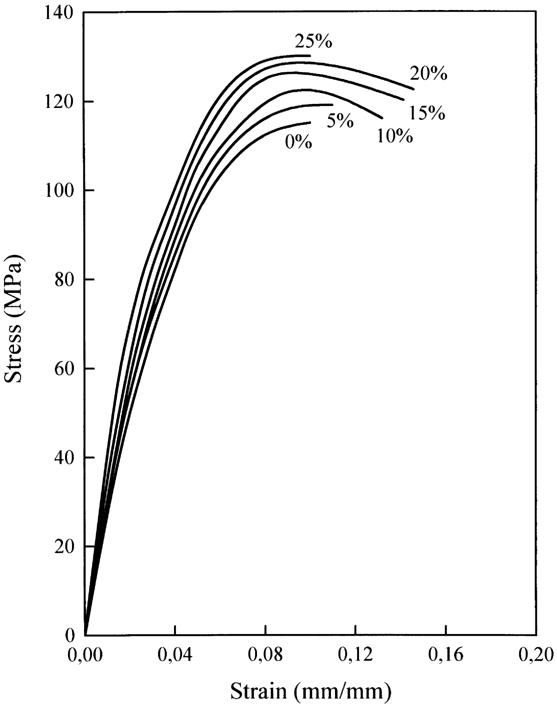

Fig. 1. Typical stress–strain curves of the mixtures containing several amounts of PSU.

instrument equipped with 3 columns PLGel of 500, 10^4 and 10^6 Å, from Polymer Labs.

Mixtures were made by solving the resin in a 10 wt.% solution containing the desired amount of PSU in dichloromethane. After removing the solvent by heating at 80°C in vacuum, DDM in a stoichiometric amine/epoxy ratio was added by continuously stirring the mixture for 5 min. In the case of mixtures with 20 and 25 wt.% PSU, mixing was made at 100°C. Some bubbles could not be removed for the 25 wt.% PSU-containing mixture. All blend solutions were transparent at this stage, indicating complete miscibility.

In order to study the final properties of the mixtures modified with different amounts of PSU, they were poured into a preheated mould at 100°C, and cured for 100 min and then degassed in vacuum for 30 min. In the case of the 15 wt.% PSU-containing mixture, precuring was also carried out at different temperatures and curing times (60°C, 540 min; 80°C, 150 min; 100°C, 100 min; 120°C, 60 min; 140°C, 60 min; 160°C, 60 min) using vacuum during the first stages of curing. Afterwards, all mixtures were post-cured at 200°C for 2 h, allowing them to cool gradually to room temperature. Neat PSU was moulded in a compression press for comparison.

Transmission optical microscopy (TOM) measurements were performed with a Olympus BHT-M equipment. The epoxy/PSU binary mixtures were dynamically studied up to 200°C. For ternary systems, scans were carried out isothermally at the temperatures used for precuring the mixtures.

Scanning electron microscopy (SEM) studies have been performed with a Hitachi S-2700 scanning electron microscope with an accelerating voltage of 15 kV. After overnight etching with dichloromethane for thermoplastic removal, fracture surfaces were coated with an Emscope SC500 gold sputterer.

Rheological properties were characterized by dynamic mechanical analysis using a Metravib viscoanalyser, and working isothermally in annular shearing at a frequency of 10 Hz. The specimen size was usually 4 g.

Differential scanning calorimetry (DSC) dynamic mode measurements were carried out with a Perkin–Elmer DSC-7 (in a dry nitrogen atmosphere and calibrated with an indium standard) working with 6–8 mg samples in aluminum pans. Runnings at a constant heating rate of 10°C min^{-1} were performed in a temperature range of 30–250°C for every mixture. The heat evolved during the reaction of the mixtures has been directly determined by the integration of the exothermic peaks. The glass transition temperature, T_g, was taken in a second scan as the beginning point of the endothermic shift in the DSC scan.

The dynamic mechanical thermal (DMTA) behavior of the neat and modified epoxy mixtures was studied in the same viscoanalyser in a three-point bending device from 20 to 250°C at 3°C min^{-1} and 10 Hz, using $60 \times 12 \times 5\ \text{mm}^3$ specimens. The temperature corresponding to the maximum for the α relaxation, $T\alpha$, in the loss factor plotting was also recorded as a measurement of the glass transition temperature. The rubber modulus, E'_r, taken as the modulus at $T\alpha + 40$°C, was used to compare the cross-link density of the networks.

Mechanical measurements were performed in a Instron 4206 test machine equipped with a 5 kN load cell. Flexural tests were carried out at room temperature according to the ASTM D-790 standard at a cross-head rate of 1.7 mm min^{-1} using $80 \times 12 \times 5\ \text{mm}^3$ specimens. As shown in Fig. 1, typical stress–strain curves indicate that, with an exception to the 25 wt.% PSU containing sample which broke at yield, the PSU-modified mixtures yielded. Fracture toughness tests were made following the European Structural Integrity Society (ESIS) protocol [23,24] using single-edge-notched type samples ($60 \times 12 \times 5\ \text{mm}^3$) in a three-point bending geometry. For both tests, a minimum of five specimens were used. The critical stress intensity factor, K_{Ic}, and the critical strain energy release rate, G_{Ic}($G_{Ic} = (1 - \nu^2)K_{Ic}^2/E$), where ν is the Poisson's ratio, taken as a 0.35 value, and E is the average flexural modulus for each composition), were calculated in this way.

3. Results and discussion

Initially, in order to analyze the cure kinetics thereafter, the potential interactions existing between the curing agent and the thermoplastic have been studied by Fourier transform infrared (FTIR) spectrometry in a Perkin–Elmer machine, model 16 PC, by using KBr plates. As shown in

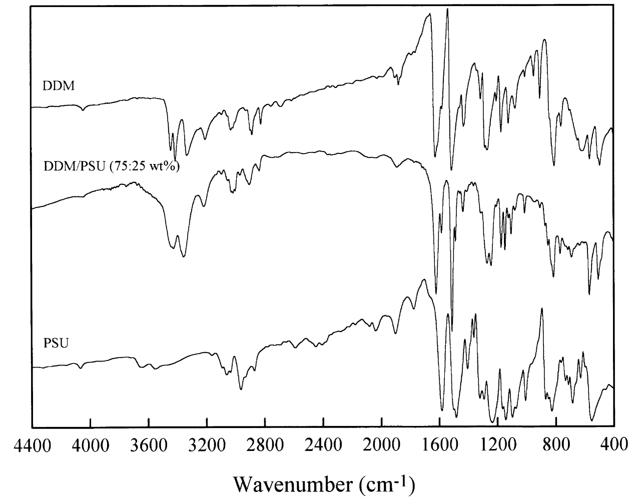

Fig. 2. FTIR spectra for DDM, PSU and DDM/PSU mixture after 1 h at 140°C.

Fig. 2 for the DDM/PSU (75:25 wt.%) mixture, no significant peak variations with respect to those of the corresponding neat compounds, were observed after thermal treatment at 140°C for 1 h. On the one hand, though not shown, significant variations were neither observed for the binary DGEBA/PSU mixture after treatment during 1 h at 140°C. These results show that chemical reactions with PSU did not occur during curing of the resin–hardener mixture. On the other hand, for the mixture containing PSU and DDM, the band centred around 3220 cm^{-1}, corresponding to the primary amine groups of the hardener, did not change in frequency, because the extent of physical interactions with the thermoplastic was not remarkable. This behavior differs from that found for other epoxy mixtures such as PMMA-modified ones, for which variations in absorption frequency have been presented as a consequence of interactions with the curing agent used in the epoxy mixture [25].

As studied by optical microscopy, the epoxy resin and the PSU were fully miscible in the 20–200°C range for all the PSU contents used in the ternary blends investigated. This behavior agrees with the high lower critical solution temperatures (LCST) reported by Moller et al. [21] for the

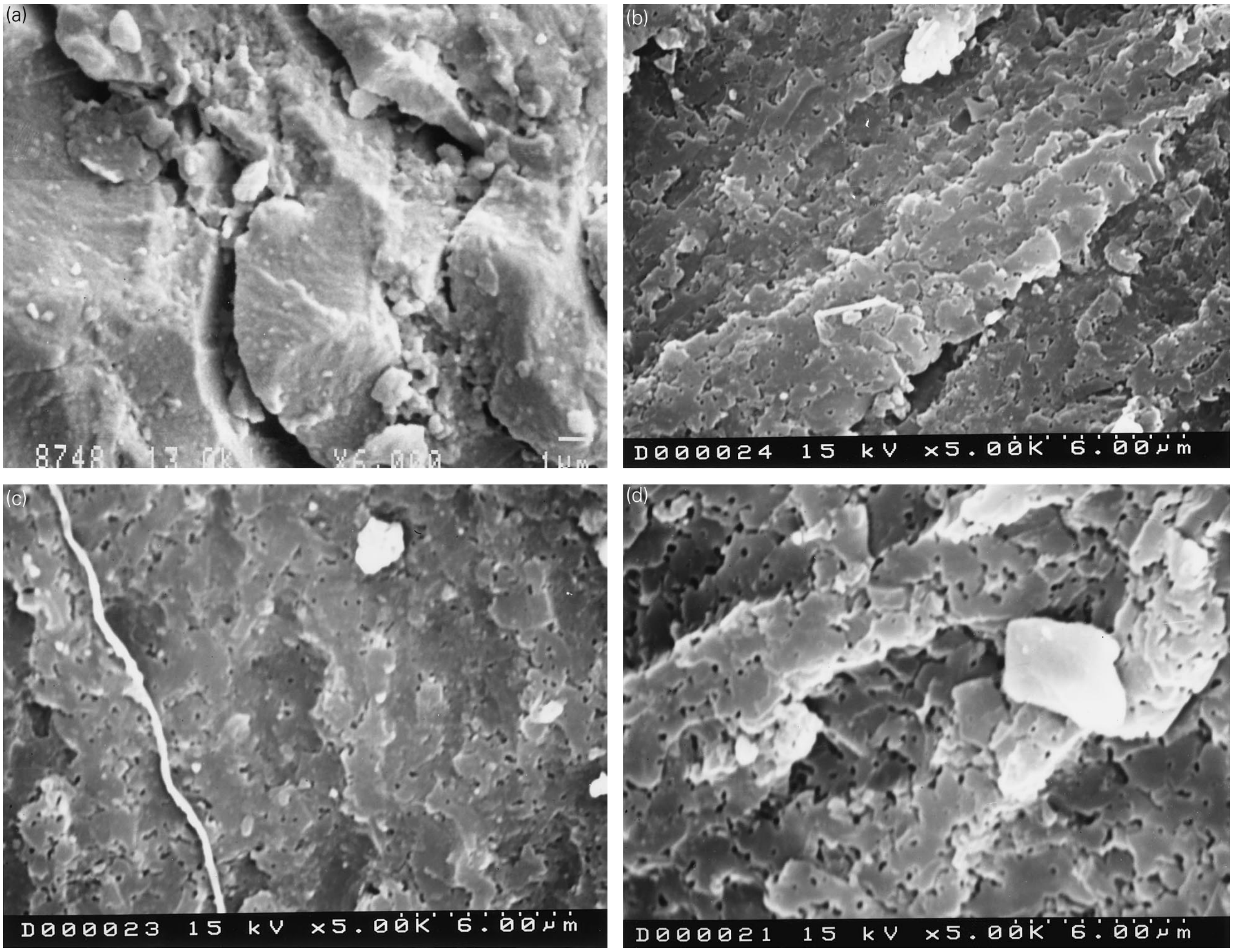

Fig. 3. SEM micrographs for mixtures containing 15 wt.% PSU precured at several temperatures: (a) 60; (b) 100; (c) 120; and (d) 160°C.

PSU containing similar epoxy mixtures using model compounds. On the other hand, for the temperature range (60–160°C) used for precuring the ternary mixtures containing a 15 wt.% PSU, some translucity was clearly observed, but only for the mixture polymerized at 160°C. In the same way, the phase separation behavior of stoichiometric mixtures modified with several percentages of PSU (from 5 to 25 wt.%) was also investigated by maintaining them for 2 h at 100°C. As shown below by rheological measurements, this period at 100°C was enough for vitrification to happen. Mixtures appeared slightly translucent only for PSU contents higher than 15 wt.%.

Complementarily, with the object of ensuring the miscibility existing in the cross-linked mixtures, SEM studies were also performed for mixtures containing 15 wt.% PSU precured at different temperatures. As presented in Fig. 3(a)–(d), similar results to those obtained by Moller et al. [21] were obtained for mixtures precured at temperatures equal or higher than 100°C, as very small spherical particles ($\varnothing \cong 0.20 - 0.30\ \mu m$) were formed dispersed into the epoxy matrix indicating that phase separation possibly occurred via a binodal mechanism. The small size of the discrete particles, with a unimodal distribution, which increased slightly with precure temperature, seems to indicate that phase separation started in the gelation region, so that particle growth was not possible because of the diffusional restrictions existing after gelation of the epoxy matrix.

As shown in Fig. 3(a), no phase-separation insights were detected for the sample precured at 60°C possibly because vitrification of the polymerizing resin mixed with the thermoplastic, occurred before chemical gelation at this precuring temperature, therefore, increasing the solution viscosity, and thereafter the high polymerization rate in the post-curing stage arrested demixing.

Moreover, SEM studies were also carried out for

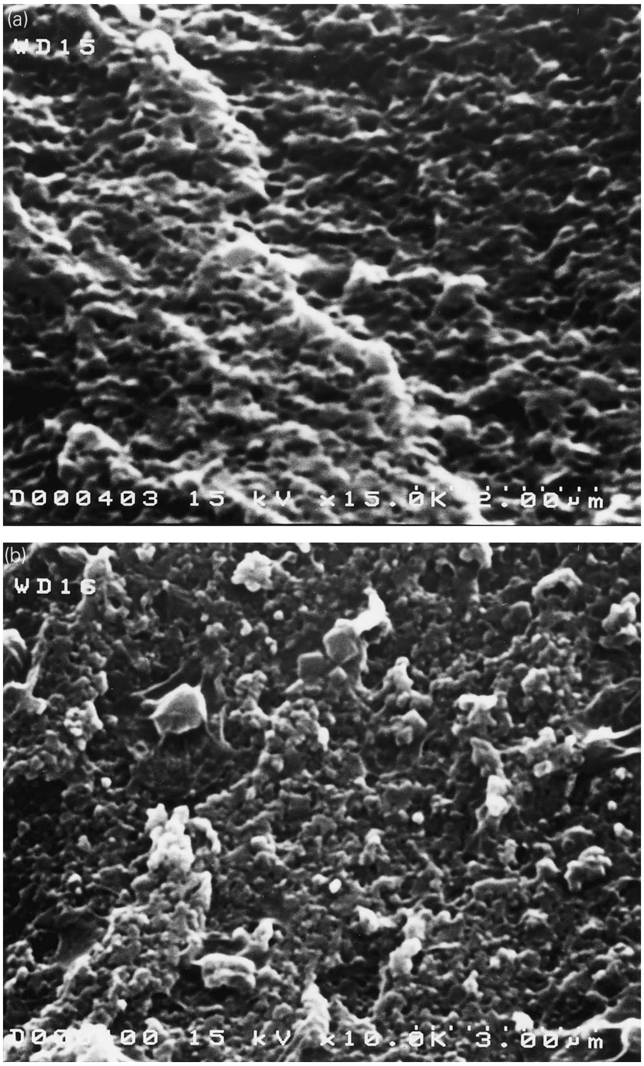

Fig. 4. SEM micrographs for modified mixtures containing 20 and 25 wt.% PSU precured at 100°C: (a) 20; and (b) 25 wt.%.

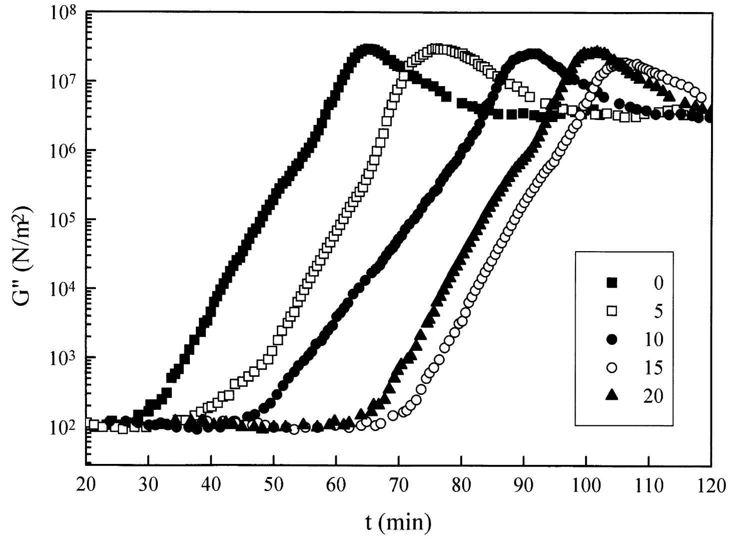

Fig. 5. Loss modulus variation vs. cure time at 100°C as a function of PSU content.

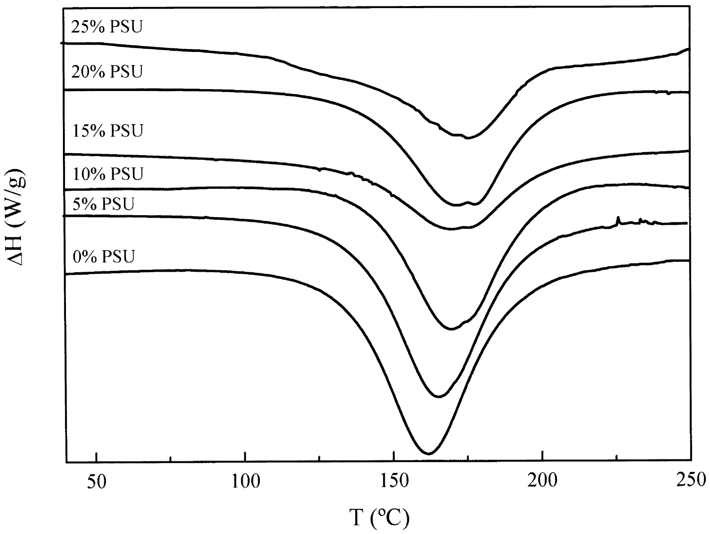

Fig. 6. Thermal scans obtained by dynamic DSC for mixtures with several PSU contents.

modified mixtures containing 20 and 25 wt.% PSU, and precured at 100°C. The corresponding micrographs are reported in Fig. 4(a) and (b), respectively. For the 20 wt.% PSU containing mixture, some microdomains of the dispersed phase were interconnected. This interconnectivity increased for the mixture modified with 25 wt.% PSU, for which some thermoplastic-rich regions had very small epoxy particles inside.

Rheological measurements carried out in a viscoanalyser at 100°C permitted the characterization of gelation and vitrification processes during curing. From Fig. 5, in which the evolution of the loss modulus, G″, is plotted against curing time and the delay produced in both physical phenomena (gelation corresponds to the clear increase in G″, vitrification to the G″ maximum) by PSU addition becomes evident, as the corresponding times clearly increased with respect to those for the neat epoxy matrix and above all for thermoplastic amounts higher than 10 wt.%. This delay can be attributed to the dilution effect exerted by the thermoplastic and also to the viscosity increase produced by PSU addition.

As shown in Fig. 6 for the variation of the temperature corresponding to the exotherm peak, T_{peak}, upon PSU content, the delay in the cure kinetics was confirmed by thermal measurements performed at 10°C min^{-1}. Nevertheless, PSU apparently did not modify the mechanism of the epoxy matrix polymerization as the total enthalpy, ΔH, shown in Table 1, decreased proportionally to the PSU amount in the mixture. So, and taking in to account that physico-chemical interactions were not detected by FTIR measurements, the delay in polymerization should mainly correspond to physical reasons such as dilution effect or viscosity increase because of the PSU addition. It is worth noting that a small shoulder, more evident for higher PSU contents, was detected for all the modified mixtures after the exotherm peak appeared. In the same way as for the same epoxy matrix modified with poly(methyl methacrylate) [16], this peak can be attributed to the phase separation which occurred in the high temperature range of dynamical scannning due to the mobility comparable to that existing in the high precure temperature isothermal curing.

Thereafter, the thermal behavior of the modified mixtures fully cured was also analyzed by DSC measurements. As shown in Tables 1 and 2 for the mixtures investigated by DSC in the second scan (after the dynamic one carried out for the uncured mixtures up to 250°C) and for those polymerized with the cure schedule used, respectively, the T_g of the modified mixtures containing 15 wt.% PSU or less was similar to that corresponding to the neat epoxy and pure PSU. On the contrary, the T_g of the 20 and 25 wt.% PSU-modified mixtures, but above all for the higher PSU content, was clearly lower than that for the other mixtures, thus

Table 1
Thermal properties of PSU-modified epoxy mixtures. T_g values correspond to the second running after a dynamic scan up to 250°C

PSU (%)	T_{peak} (°C)	ΔH (J g^{-1})	T_g (°C)
0	160	425	176
5	167	420	177
10	169	405	177
15	171	411	178
20	171	375	163
25	175	353	158

Table 2
Thermal properties of PSU-modified epoxy mixtures polymerized with the cure schedule

PSU (%)	0	5	10	15	20	25	100[a]
T_g (°C)	179	185	184	185	178	175	184

[a] Processed by compression.

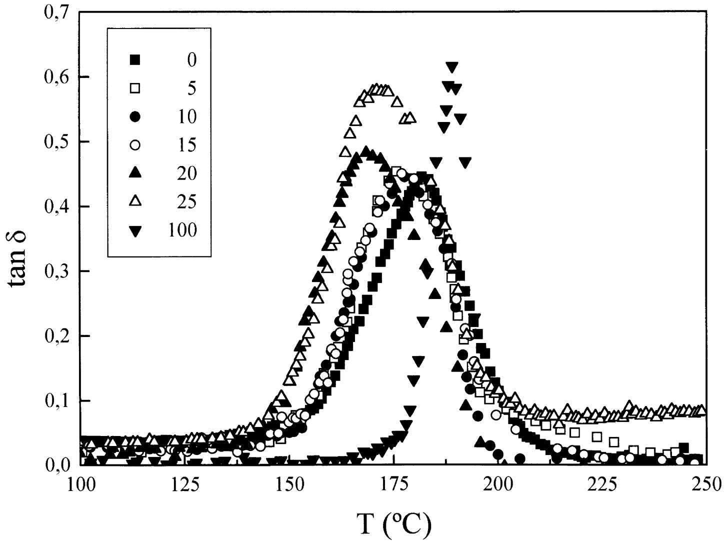

Fig. 7. DMTA behavior of epoxy matrices with different contents of PSU (scale for neat PSU is up to 1.5).

indicating that some epoxy oligomer migrated to the thermoplastic-rich phase. The clearly lower T_gs observed for the dynamically scanned PSU-modified mixtures with respect to those for the polymerized with the cure schedule, outlines the importance of the control of cure temperature. Thus, the differences shown in T_g values quoted in Tables 1 and 2 for the mixtures cured by the above referred ways would be connected to distinct levels of segregation through phase separation during the dynamic curing, and during polymerization with the cure schedule.

As shown in Fig. 7, similar results were observed when analysis was performed by DMTA. Thus, both neat matrix and mixtures containing as much PSU as 15 wt.% presented a α relaxation in the same temperature range. For mixtures with a higher amount of PSU, the left side of the α relaxation appeared at lower temperatures as the PSU amount increased. This behavior corresponded well with the morphology presented above for the 20 and 25 wt.% PSU phase-separated mixtures, for which the thermoplastic phase did not appear as discrete particles. For these mixtures, phase separation became more evident possibly because of some differential segregation in one of the components to the PSU-rich phase. This segregation could cause some stoichiometrical imbalance in the epoxy matrix, thus decreasing its T_g.

In the same way, these techniques were also used to study the compatibility in the fully cross-linked mixtures modified with a 15 wt.% PSU and precured at different temperatures. In the same way as observed by SEM, the DMTA scans reported in Fig. 8 indicated that the mixtures precured at temperatures lower than 100°C, but above all the one precured at 60°C, presented a higher α relaxation and

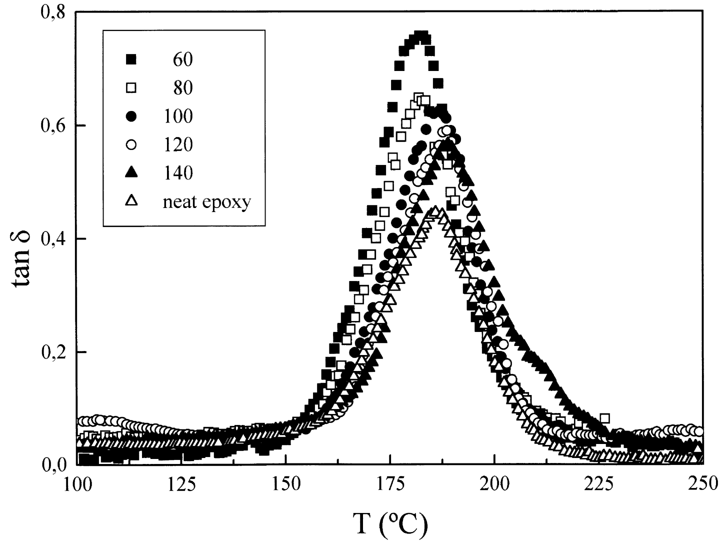

Fig. 8. DMTA behavior of epoxy matrices containing a 15 wt.% PSU and precured at different temperatures (neat epoxy matrix has been precured at 100°C).

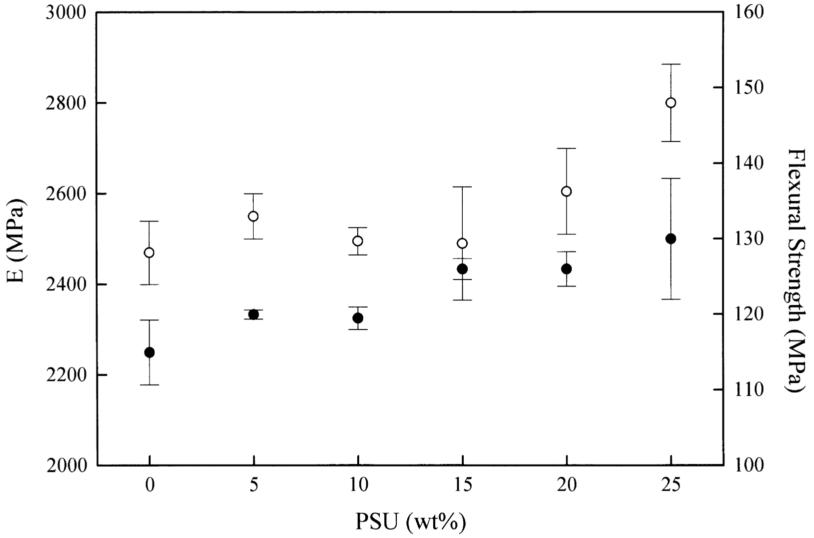

Fig. 9. Flexural properties of epoxy matrices with different contents of PSU: (○) modulus; and (●) strength.

appeared at slightly lower temperatures than for the other precure temperatures used. This fact corroborates the apparent miscibility of the mixture moulded at these conditions. As shown above, T_g measurements carried out by DSC showed similar trends. These results, together with those obtained for mixtures containing different amounts of PSU, confirm the need to refer to the cure conditions when compatibility investigations are carried out in modified thermosetting mixtures as a consequence of both thermodynamic and kinetic factors controlling the final state of these mixtures.

The influence of thermoplastic addition in mechanical behavior was also studied. With the exception of the neat mixture, all mixtures yielded before cleavage. Fig. 9 presents the small-deformation mechanical properties of these materials. The inclusion of the higher rigidity PSU in the epoxy matrix led to a small increase in flexural modulus. This increase was more pronounced for the mixtures containing more than 15 wt.% PSU as a consequence of the near inter-connected PSU-rich phase existing for these compositions which, because of the higher elastic modulus of PSU, increased the elastic modulus of the mixture. In the same way, the small particles segregated from the epoxy matrix at low PSU amounts did not influence practically the yield strength of these materials, but the change in morphology occuring at high modifier contents produced an increase in the strength of the corresponding mixtures.

As shown in Fig. 10, the apparent miscibility existing for the 15 wt.% PSU-modified mixture precured at 60°C led to higher rigidity and strength than that observed for the same

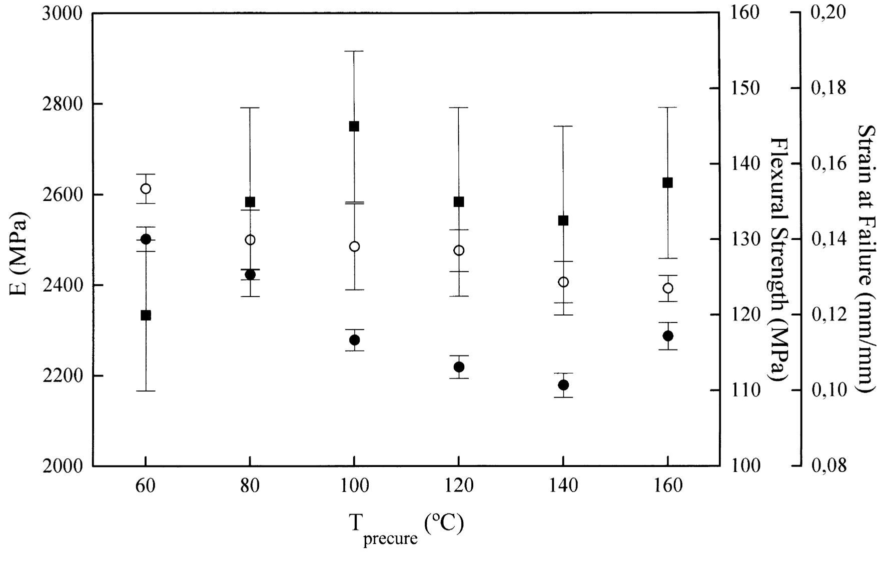

Fig. 10. Flexural properties of epoxy matrices containing a 15 wt.% PSU and precured at different temperatures: (○) modulus; (●) strength; and (■) strain at failure.

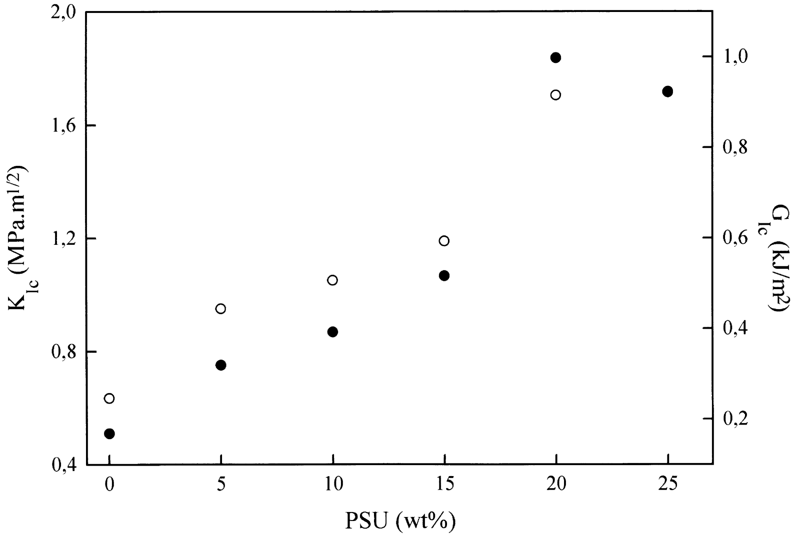

Fig. 11. Fracture toughness of epoxy matrices with different contents of PSU: (○) K_{Ic}; and (●) G_{Ic}.

mixtures precured at other temperatures as a consequence of phase separation happening through curing in the latter ones. It is worthnoting that phase separated mixtures were more deformable than that precured at 60°C.

Finally, the fracture toughness was also investigated for mixtures with different amounts of PSU and also for 15 wt.% PSU-modified ones precured at different temperatures. As reported in Fig. 11, thermoplastic addition only led to a small improvement in fracture properties as K_{Ic} and G_{Ic} at low PSU contents, but the increase in G_{Ic} was around five-fold for percentages higher than 15 wt.% PSU, because of the near bicontinuous morphology shown by these mixtures.

In connection with the compatibility of the mixtures, similar trends to those observed for other properties were observed for the fracture toughness behavior of the 15 wt.% PSU-modified systems precured at different temperatures. Thus, as shown in Fig. 12, the lower G_{Ic} for the mixture precured at 60°C was a consequence of its apparent miscibility since, as is well known nowadays, phase separation is a boundary condition for toughness improvement in modifier-containing thermosetting mixtures.

4. Conclusion

Several physico-chemical and morphological techniques have been used to elucidate the controversy existing about the miscibility of PSU-modified epoxy matrices cured with an amine such as DDM.

PSU addition causes a delay in polymerization of the epoxy matrix. This delay can be attributed in the analyzed mixtures to both dilution effects and viscosity increase as a

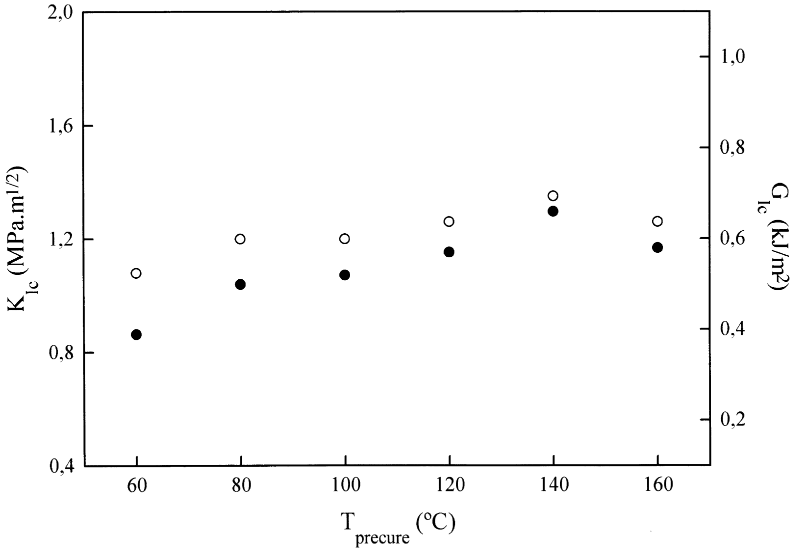

Fig. 12. Fracture toughness of epoxy matrices containing a 15 wt.% PSU and precured at different temperatures: (○) K_{Ic}; and (●) G_{Ic}.

consequence of thermoplastic addition, since no evident interactions or chemical reactions were observed between the components of the mixtures.

It has been proved that these epoxy matrices are immiscible but kinetic factors can arrest the phase separation. Control of the morphology can be performed only by varying the processing temperature. Mixtures precured at high temperatures containing PSU percentages equal or higher than 15 wt.% were translucent as a result of phase separation. The importance of the control of the precure temperature in the final morphology of the modified mixtures has been proved. Thus, for the 15 wt.% PSU containing mixtures, complete transparency or translucity can be obtained as a function of cure conditions.

For a given thermoplastic amount, the increase of immiscibility lowers the rigidity and the strength but increases the fracture toughness of the PSU-modified epoxy matrices. These properties, above all fracture toughness, are also dependent upon the thermoplastic percentage, and the subsequent morphology formed, in the mixture. The higher fracture toughness is reached for a practically bicontinuous morphology.

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