

Control of morphologies and mechanical properties of thermoplastic-modified epoxy matrices by addition of a second thermoplastic

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Abstract: Ternary mixtures based on stoichiometric mixtures of the diglycidyl ether of bisphenol-A (DGEBA) and 4,4'-diaminodiphenyl sulfone (DDS) and two miscible thermoplastics, poly(methyl methacrylate) (PMMA) and the poly(hydroxy ether of bisphenol-A) (phenoxy), were investigated by optical microscopy (OM), atomic force microscopy (AFM) and dynamic mechanical analysis (DMA). Mechanical testing was used to study the ultimate behavior. All the modified epoxy mixtures were heterogeneous. DMA has been shown to be an excellent technique for detecting the morphologies generated after curing when the loss modulus is used for analysis. Morphology varied with the thermoplastic content on the mixtures. The addition of a second thermoplastic in small amounts changed the morphological features from particulated to co-continuous and from that to phase-inverted morphologies. A significant increase in fracture toughness was observed above all for the mixtures with some level of co-continuity within the epoxy-rich matrix. Phase inversion led to poor strength and also fracture toughness.

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Keywords: epoxy modification; poly(methyl methacrylate); phenoxy; morphology; mechanical properties

INTRODUCTION

Thermoplastic (TP) modification of brittle thermosetting matrices has been used successfully to enhance the fracture toughness but retaining the thermal stability of the thermoset.^{1–6} Reaction-induced phase separation through epoxy curing is advantageous in this context. A variety of morphologies can be generated by an adequate selection of cure cycles and initial formulations.^{7–9} In order to reach significant toughness enhancement, strong polymer–polymer interfacial adhesion between the separated phases has been claimed to be necessary in earlier studies.^{10–12}

Morphology is a significant factor influencing the mechanical properties of modified epoxy mixtures.^{13–15} Concentration, molar mass and chemical features of the modifier, and also cure rheokinetics at the set cure temperature, are key factors controlling the particulate, bicontinuous or inverted morphologies that can be generated. For thermoplastic modification, a significant improvement of fracture properties is usually only obtained for the unparticulated microstructures owing to the poor adhesion between the phases.¹⁶ Thereby, in order to satisfy the growing demands for tough and rigid thermosetting matrices

with good thermal and chemical performances, new ways of modification are being investigated. It is considered that the compatibilization of polymer blends is of great importance in controlling the performance of polymer alloys. In the same way, the emulsifying activity of block copolymers widely used for compatibilizing immiscible thermoplastic blends^{17–21} has recently been applied to improve the mechanical properties of thermoplastic–epoxy blends.^{16,22} Another possibility, which has been considered to only a limited extent,^{23–26} is the simultaneous addition of two polymers to the thermosetting resin before curing. In this way, many different morphologies could result, depending on the miscibility and diffusivity²⁷ between the modifiers and between them and the epoxy matrix.

We have previously demonstrated^{9,14,28} that the morphologies of poly(methyl methacrylate) (PMMA)-modified epoxy matrices are strongly dependent on the PMMA content and also on curing conditions, as a consequence of competition between thermodynamic and kinetic factors. From an initially homogeneous solution, we were able to tailor polymer mixtures ranging from opaque to transparent with different mechanical properties depending on the curing

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conditions. The curing agent also has a great influence on the morphology, since it also influences both the thermodynamics and the cure kinetics of the mixtures.^{28–33}

As for other epoxy matrix blends, poly(hydroxy ether of bisphenol-A) (phenoxy) addition can also lead to phase-separated or homogeneous systems as a consequence of variations in physico-chemical interactions but also due to viscosity differences when the curing agent is changed. Thus, miscibility has been reported for phenoxy-modified epoxy networks for curing agents such as some aromatic amines (4,4'-diaminodiphenylmethane (DDM)) and anhydrides.^{34,35} Also, immiscibility was found in the literature survey for epoxies cured with aromatic amines, such as 4,4'-diaminodiphenyl sulfone (DDS).^{30,35–37} Even for the same amine, DDS, transparent, homogeneous and opaque, and also inhomogeneous epoxy–phenoxy mixtures have been described³⁶ through kinetic control of the curing rate.

The present study was intended to investigate the simultaneous modification of an epoxy matrix with two thermoplastics. Both morphological variations and their influence on the mechanical and fracture properties of immiscible PMMA-modified DGEBA–DDS epoxy matrices occurring by incorporation of another amorphous thermoplastic such as phenoxy were investigated. Phenoxy–PMMA blends form a single-phase mixture in the melt.^{38–41} The influence of the thermoplastic matrix on the ultimate mechanical behavior was also analyzed for mixtures in those the thermoplastic becomes the dominant phase. Morphologies were investigated by atomic force microscopy (AFM), and the results were compared with those obtained from dynamic mechanical analysis (DMA). Finally, the effects of morphological variations on flexural properties and fracture toughness were also analysed.

EXPERIMENTAL

The epoxy resin DER 332, kindly supplied by Dow Chemical, was a diglycidyl ether of bisphenol-A (DGEBA). It has an epoxy equivalent weight of around 175. DDS curing agent (Fluka quality) was used in a stoichiometric amine/epoxy ratio for all mixtures. The selected thermoplastics were PMMA, Lucryl G77 (BASF) and phenoxy, PKHH (Paphen Phenoxy Associates), with $M_n = 42\,800$, $M_w = 82\,300$ and $M_n = 25\,800$, $M_w = 56\,700$, respectively, as determined by gel permeation chromatography with polystyrene standards.

Ternary epoxy blends containing several concentrations of PMMA + phenoxy, with variable ratios of both thermoplastics (TP) (as an example, 10:5 PMMA–phenoxy means 10 wt% PMMA and 5 wt% phenoxy were added to the epoxy–amine system), were prepared according to the following procedure. The mixture of thermoplastics was first dissolved in dichloromethane to give an approximately 10 wt% solution and then DGEBA was added. After the

solvent had been removed by heating at 110 °C for 8 h and further overnight degassing *in vacuo*, DDS in a stoichiometric amine/epoxy ratio was added while stirring the mixture for 5 min at 135 °C. At this stage, all mixtures were transparent, thus indicating complete miscibility. These mixtures were poured into a preheated mould at 135 °C and cured for 6 h, degassing with vacuum during the early stage of curing. The mixtures were then post-cured at 200 °C for 2 h and thereafter allowed to cool gradually to room temperature.

Phase separation during polymerization at 135 °C was followed using an Olympus BTH-M optical microscope (OM) with a Mettler FT 82 heating chamber. Samples for analysis were placed between two glass slides. The same optical microscope was used for the analysis of the fractured surfaces.

The dynamic mechanical behavior of the neat and modified epoxy mixtures was analyzed using a Metravig viscoanalyzer from 20 to 250 °C at 3 °C min⁻¹ and a frequency of 10 Hz in a bending device. The specimen size was 60 × 12 × 5 mm. The data were recorded in the form of storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) as a function of temperature. The temperature corresponding to the maximum for the α relaxation in the loss factor was recorded as the glass transition temperature, T_g . The same viscoanalyzer was used for following cure rheology by using an annular pumping device. The loss factor shows two maxima through curing: the first occurs in the region where both storage and loss moduli suddenly increase as gelation takes place, and the other appears at longer times as vitrification occurs.

Morphological investigation was undertaken on the broken specimens of fracture toughness tests by using a Nanoscope IIIa AFM (Digital Instruments). Measurements were performed by operating in the contact mode (the tip was always touching the surface when the feedback loop was on) in air, using commercial silicon nitride probes with V-shaped cantilevers of 200 nm length and spring constant 0.12 N m⁻¹, and with a tip of a nominal curvature radius of 5–10 nm. Images are presented without any image processing except horizontal leveling. Phase imaging was used as a contrast enhancement technique.

Mechanical tests were performed in an Instron 4206 test machine equipped with a 1 kN load cell. Flexural properties were measured at room temperature according to the ASTM D790M standard at a crosshead rate of 2.1 mm min⁻¹ using 100 × 10 × 5 mm specimens. Fracture toughness tests were performed following the protocol of the European Structural Integrity Society (ESIS)^{42,43} using single-edge-notched type samples (60 × 12 × 5 mm) in a three-point bending geometry. Both the critical stress intensity factor, K_{Ic} , and critical strain-energy release rate, G_{Ic} , were measured. For both tests a minimum

of five specimens were used. Poisson's ratio was taken as 0.35 for all matrices.

RESULTS AND DISCUSSION

Figure 1 shows experimental curves of the intensity of transmitted light as a function of polymerization time at 135 °C for epoxy mixtures containing 10 wt% TP with several PMMA/phenoxy ratios. After some initial perturbations, the intensity remained constant at the earlier stages of curing since the mixtures were miscible and consequently transparent. As the phase-separation process began to take place, a sharp decrease in the intensity of the transmitted light occurred until the intensity reached a constant low value as the mixtures changed to an opaque state. Phenoxy separated at a slight shorter time than PMMA. For modification with a 10 wt% of a mixture of both thermoplastics with a 5:5 PMMA/phenoxy ratio, phase separation started at a similar time to that shown for modification with phenoxy. Cure behavior was followed by analyzing the loss factor, $\tan \delta$, vs time variation at the same cure temperature in a Metravig viscoanalyzer using an annular pumping device. As seen in Fig 1, for all mixtures phase separation occurred before matrix gelation, measured as time to the first maximum on the loss factor.

Morphologies of epoxy mixtures modified with one thermoplastic

Morphological analysis was performed on DGEBA–DDS mixtures modified with several amounts of PMMA or phenoxy. As shown previously by other workers, in the case of PMMA-modified mixtures, Fig 2(a)–(c), the morphologies of the fractured surfaces changed with the thermoplastic content. Thus, for the 5 wt% thermoplastic-containing mixture, small PMMA spherical domains (0.3–1.0 μm in diameter) in a continuous epoxy matrix can be seen by AFM. As shown by OM, in the same way as

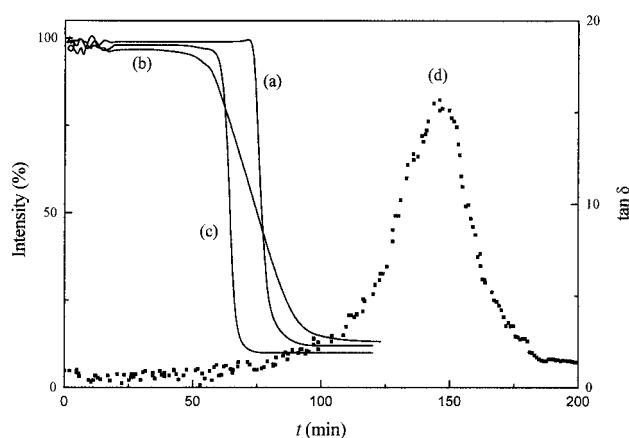


Figure 1. Intensity of the transmitted light as a function of polymerization time at 135 °C for epoxy mixtures containing 10 wt% thermoplastic with several PMMA/phenoxy ratios: (a) 10:0; (b) 0:10; (c) 5:5; (d) Loss factor vs time curve for the matrix modified with 10 wt% PMMA.

shown by Ritzenthaler *et al*,³³ at 10 wt% PMMA, the morphology becomes co-continuous, showing a complex structure with small PMMA nodules in the epoxy matrix and PMMA regions containing epoxy sub-inclusions. Finally, at 15 wt% PMMA, an apparent shift in the phase continuity was observed as the PMMA-rich phase became the matrix, the epoxy-rich phase appearing as big nodules (around 15 μm in diameter), as seen in the AFM image. This morphology is typical for modifier contents slightly beyond the critical composition.

Dynamic mechanical analysis (DMA) was first carried out on the fully cured epoxy mixtures modified with one thermoplastic to investigate further the morphologies observed by microscopy. The results are reported in Fig 3 for binary epoxy–PMMA mixtures containing various contents of PMMA. All modified epoxy mixtures showed two distinct relaxations on the E'' curve, one for the epoxy-rich phase, in the temperature range of that for the epoxy matrix, and the other for the PMMA-rich phase, in the region of the α relaxation of PMMA, respectively. The shape and size of these relaxations confirmed the microscopic features shown above. Thus, the lower height of the relaxation corresponding to the PMMA-rich phase in the 5 wt% PMMA-modified epoxy mixture with respect to that for the epoxy-rich phase supports the nodular morphology of this blend. On the other hand, the height similarity of both relaxations in the 10 wt% PMMA-modified epoxy mixture confirmed the existence of two nearly co-continuous phases. For the mixture with the higher amount of thermoplastic only the α relaxation in the low-temperature region was observed as the PMMA-rich phase became the matrix of the mixture.

As shown in Fig 4(a)–(d), in the case of phenoxy modification, small phenoxy-rich nodules, larger at higher thermoplastic contents, were also observed by AFM for both 5 and 10 wt% phenoxy-modified epoxy mixtures, although the broad domain size distribution for the 10 wt% content indicated that phase separation occurred by spinodal decomposition. The similarity in the domain size to that for PMMA modification at 5 wt% thermoplastic was a consequence of the closeness of the corresponding cloud-point times, above shown in Fig 1, which led to similar times for growth of the dispersed particles. As seen by optical microscopy, Fig 4(c), the 15 wt% phenoxy-modified mixture presented some phase co-continuity with phase-in-phase morphology, where irregular shaped islands of phenoxy-rich phase in the epoxy-rich matrix appeared. As shown in Fig 4(d), the AFM image of the epoxy-rich phase indicates that the size of the phenoxy-rich domains in the 15 wt%-modified mixture was relatively similar to that shown for the 10 wt% PMMA-modified epoxy mixture. From a qualitative viewpoint, this fact is connected to the higher molecular weight of PMMA, which leads to the critical composition for phase separation taking place at higher phenoxy contents with respect to that for the PMMA mixtures.

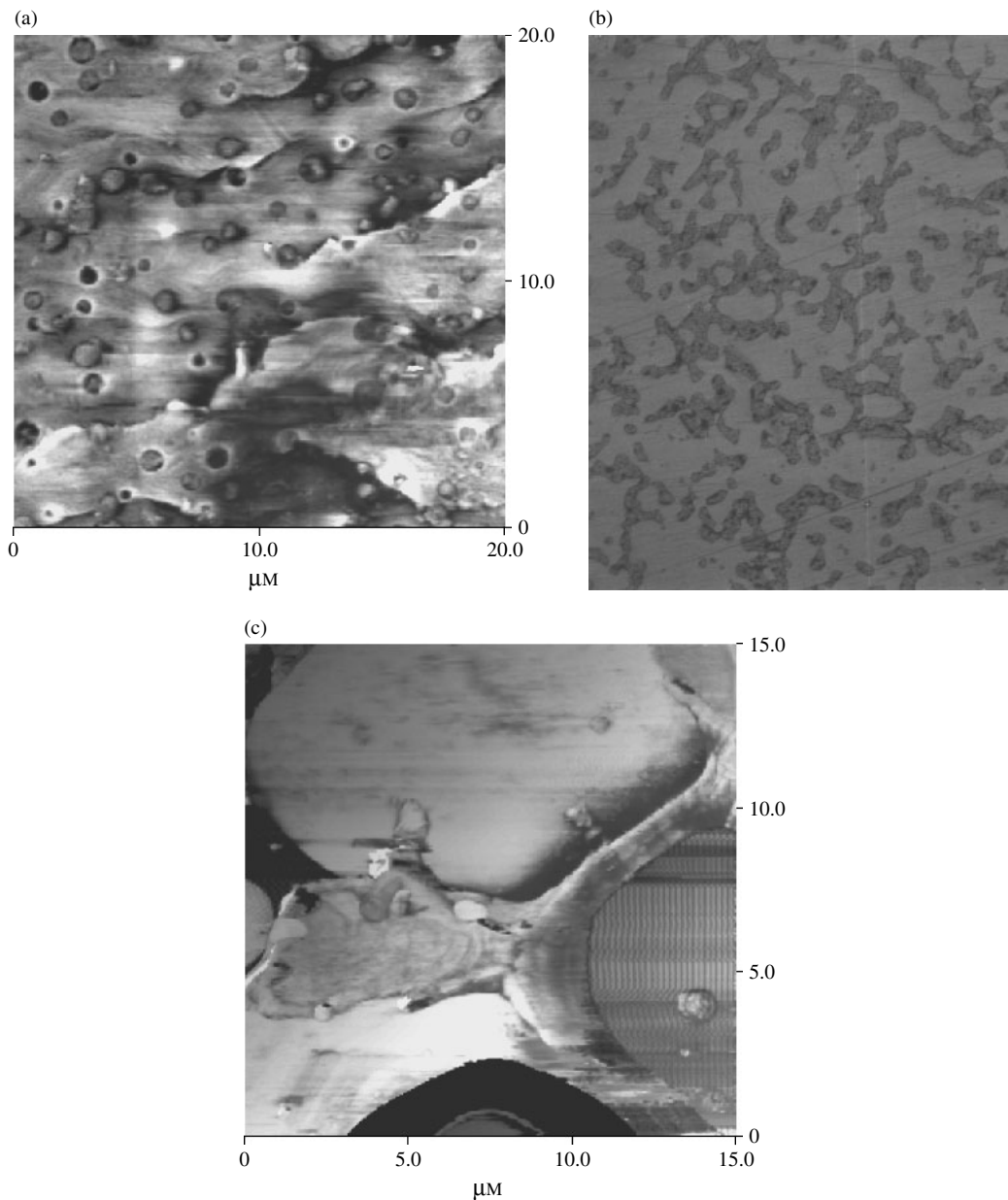


Figure 2. Micrographs of epoxy mixtures with several PMMA contents (wt%): (a) 5 (AFM); (b) 10 (OM); (c) 15 (AFM).

Figure 5 presents the dynamic mechanical spectra for the phenoxy-modified mixtures. The two-phase structure, detected by both opacity of the mixtures and microscopic images, was confirmed by this technique. Thus, in the case of the 5 and 10 wt% phenoxy-modified mixtures, the small E'' peak in the phenoxy relaxation region confirmed the existence of discrete nodules of nearly pure phenoxy in the epoxy-rich matrix. Otherwise, although no temperature variation of the relaxations was observed for the 15 wt% phenoxy content, the height increase in the relaxation corresponding to the phenoxy-rich phase with respect to that for the one of the epoxy-rich matrix is an evident probe of the beginning of co-continuity observed by OM. It is worth noting the similarity in the relaxation region of the TP-rich phase for 10 wt% PMMA- and 15 wt% phenoxy-modified systems as both mixtures presented close morphologies.

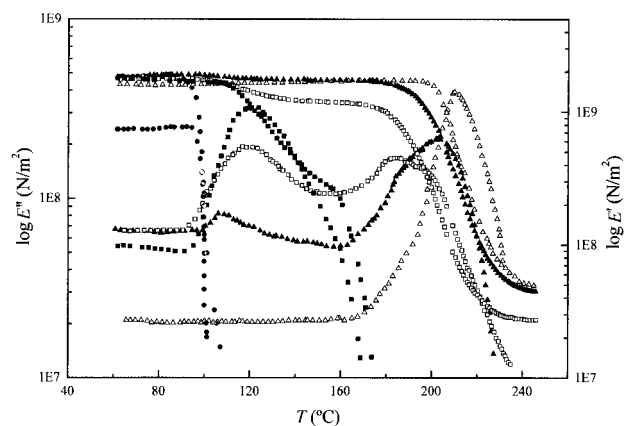


Figure 3. Loss modulus vs temperature plots for epoxy mixtures with various contents (wt%) of PMMA: (Δ) neat epoxy; (\blacktriangle) 5; (\square) 10; (\blacksquare) 15. Also included: (\bullet) neat PMMA.

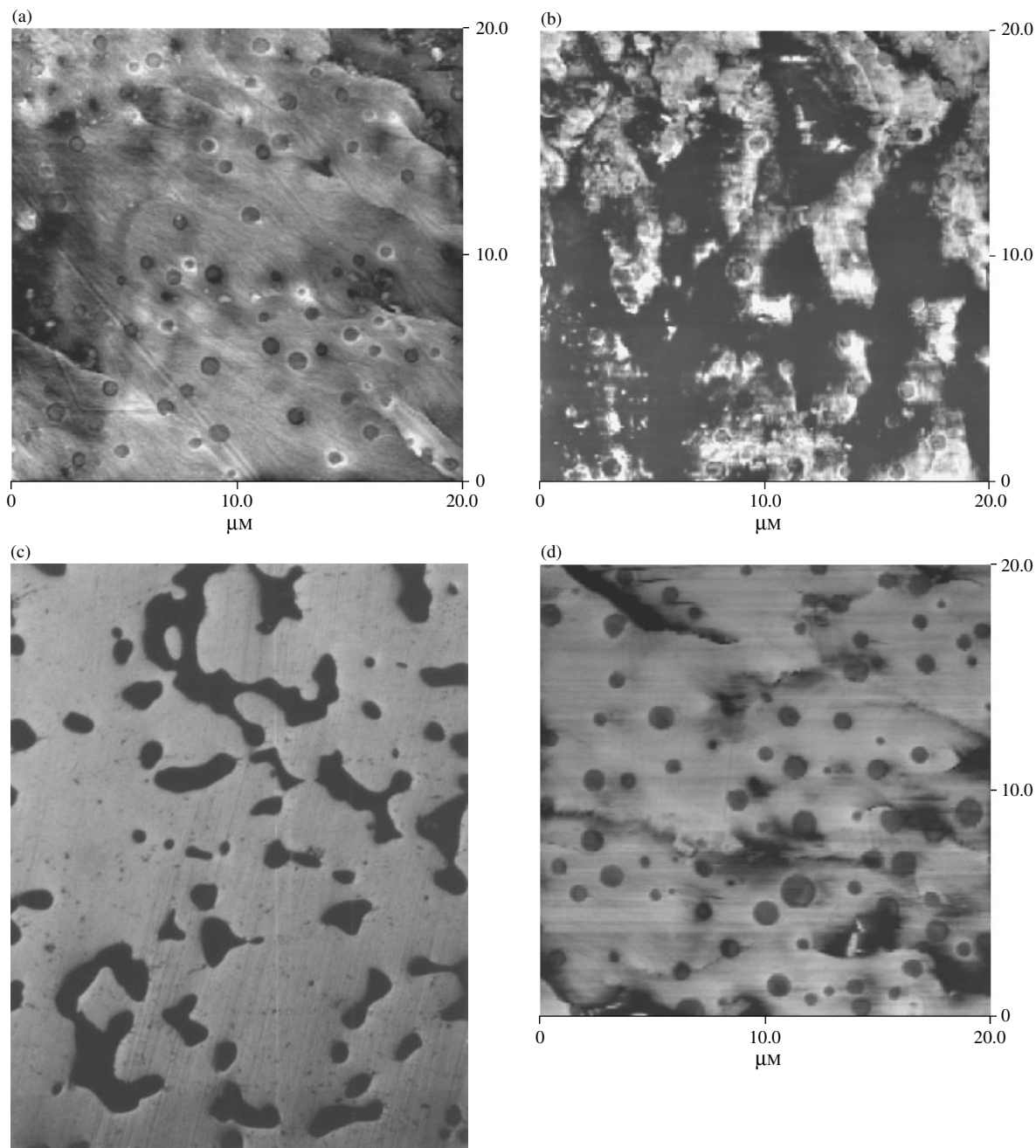


Figure 4. AFM and OM pictures of epoxy-phenoxy mixtures with various TP contents (wt%): (a) 5; (b) 10; (c) 15 (OM); (d) 15 (AFM).

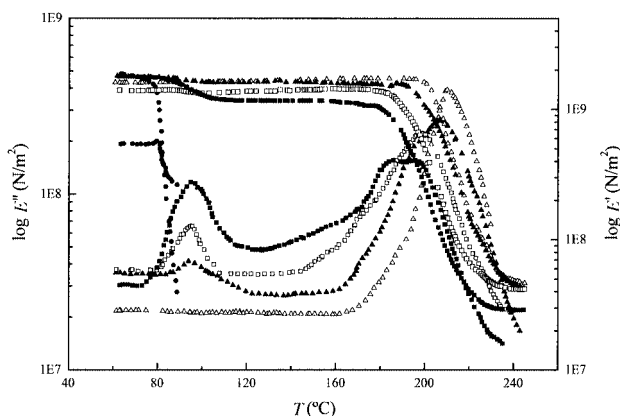


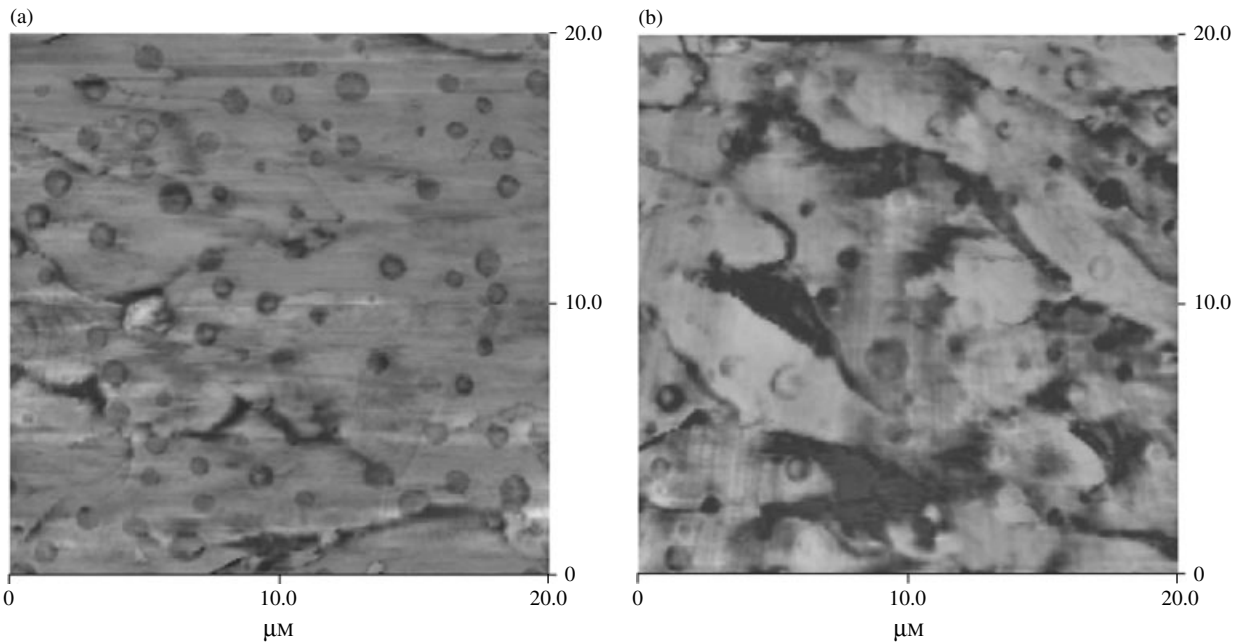
Figure 5. Loss modulus vs temperature plots of epoxy mixtures with various contents (wt%) of phenoxy: (Δ) neat epoxy; (▲) 5; (□) 10; (■) 15. Also included: (●) neat phenoxy.

As inferred from Figs 3 and 5 (see also Tables 1 and 2), modification with only one thermoplastic led to phase separation for both thermoplastics but, in the case of PMMA the glass transition of the thermoplastic-rich phase moved to higher temperatures with higher PMMA content, indicating that some cured epoxy remained in this phase for the cured mixtures. In contrast, for phenoxy modification the constancy of temperature of that relaxation indicated a nearly pure phenoxy phase-separated for all compositions.

Further, the epoxy mixtures simultaneously modified with both thermoplastics were investigated. First, the influence of phenoxy addition on the morphology of PMMA-modified epoxy mixtures was analyzed. Although not shown, for mixtures containing 5 wt%

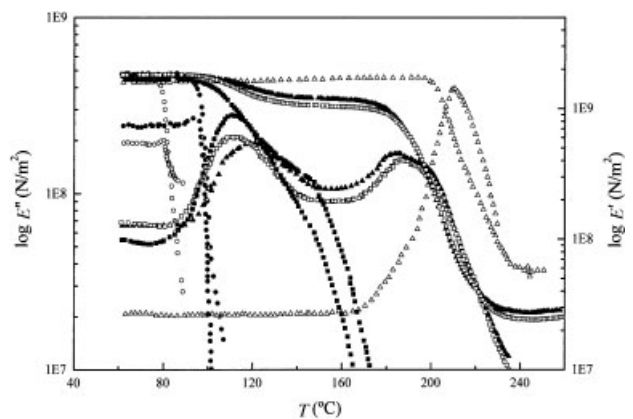
Table 1. Mechanical properties and fracture toughness of the ternary epoxy mixtures with PMMA as the main thermoplastic

PMMA (%)	Phenoxy (%)	E (MPa)	Flexural strength (MPa)	K_{IC} (MPa $m^{1/2}$)	G_{IC} (J m^{-2})	T_{g1} ($^{\circ}C$)	T_{g2} ($^{\circ}C$)
0	0	2580 \pm 20	120 \pm 1	0.81 \pm 0.10	230 \pm 30	—	224
5	0	2710 \pm 55	121 \pm 1	1.11 \pm 0.10	370 \pm 55	110	220
5	2	2690 \pm 40	130 \pm 3	1.33 \pm 0.14	585 \pm 120	96	205
5	5	3010 \pm 35	125 \pm 8	1.45 \pm 0.12	615 \pm 100	105	216
10	0	2675 \pm 30	55 \pm 5	1.54 \pm 0.20	770 \pm 200	120	212
10	2	2850 \pm 40	70 \pm 5	1.78 \pm 0.18	960 \pm 180	117	215
10	5	2550 \pm 45	88 \pm 5	1.04 \pm 0.10	375 \pm 60	122	170
15	0	2655 \pm 30	50 \pm 3	0.49 \pm 0.06	80 \pm 20	135	173

**Figure 6.** AFM micrographs of epoxy mixtures with 5 wt% PMMA for two PMMA/phenoxy ratios: (a) 5:2; (b) 5:5.

PMMA and different amounts of phenoxy, both the temperature for the E'' peak maximum of the epoxy-rich phase and especially that of the PMMA-rich phase decreased with respect to the corresponding ones in the PMMA-modified matrix without phenoxy. Taking into account that the glass transition temperature of phenoxy is slightly lower than that for PMMA, this decrease indicates that phenoxy migrates preferentially to the PMMA-rich phase, although some amount of thermoplastic should remain in the epoxy-rich phase so also decreasing the temperature of its relaxation. AFM images, Figs 2(a) and 6(a) and (b), show that the size of the particulate morphology increased slightly as the phenoxy content was increased. Although not shown, some island-like microdomains were observed in low-magnification optical microscopy photographs for the 10 wt% thermoplastic-modified mixture with a PMMA/phenoxy ratio of 5:5. This beginning of co-continuity agrees with the greater height similarity for the α relaxations of both phases and also with the storage modulus variation in the relaxation region of the TP-rich phase.

As shown in Fig 7, in the case of phenoxy addition to non-particulate 10 wt% PMMA-modified epoxy

**Figure 7.** Dynamic mechanical curves for ternary mixtures with 10 wt% PMMA for several phenoxy contents (wt%): (Δ) neat epoxy, (\blacktriangle) 0; (\square) 2; (\blacksquare) 5. Also included: (\bullet) neat PMMA; (\circ) neat phenoxy.

matrices, the height of the α relaxation corresponding to the thermoplastic-rich phase was higher than that for the epoxy-rich phase the higher was the phenoxy content in the mixture, and the peak for the epoxy-rich phase even disappeared at 5 wt% phenoxy addition. This tendency was clearly corroborated by

optical microscopy, Figs 2(a) and 8(a) and (b), as the mixtures changed from a phase-in-phase co-continuous morphology to a completely inverted structure in which the thermoplastic mixture became the continuous phase.

Concerning phenoxy-modified epoxy mixtures, PMMA addition led to slight variations with respect to that presented above for phenoxy addition to PMMA-modified mixtures. Thus, although not shown, for a 5 wt% phenoxy-modified epoxy mixture, the addition of a 2 wt% PMMA produced only small changes in the dynamic mechanical spectrum. In the case of a 10 wt% phenoxy-modified epoxy mixture, the addition of 5 wt% PMMA led to co-continuity as reflected in the corresponding dynamic mechanical spectra (not shown). These results agree with the morphological

images shown in Fig 9(a) and (b) by AFM and TOM for these mixtures.

As shown in Table 1 and Fig 10, for the mixtures modified with PMMA as the main TP, a decrease in the T_g of the thermoplastic-rich phase with respect to that for the mixtures modified with PMMA was observed as phenoxy was added. In contrast, as reported in Table 2 and Fig 11, for the mixtures modified with phenoxy as the main TP, an increase in the T_g of the thermoplastic-rich phase occurred with PMMA addition. This behavior is clear evidence of the co-existence of both polymers in the thermoplastic-rich phase. On the other hand, for PMMA-modified mixtures containing 15 wt% TP, the high T_g decrease of the epoxy-rich phase (or the high T_g increase of the PMMA-rich phase), even higher than that obtained

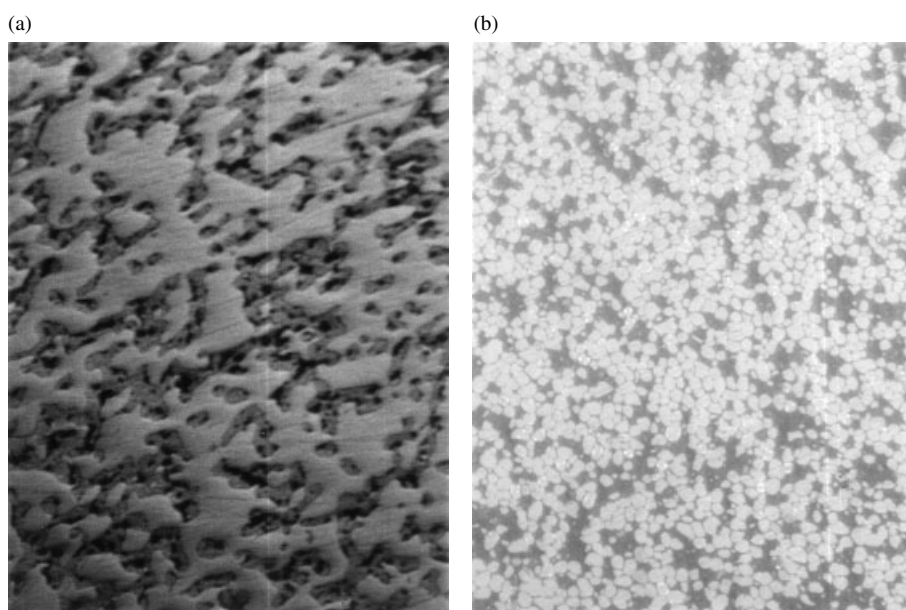


Figure 8. Optical microscopy photographs for ternary mixtures with 10 wt% PMMA for two phenoxy contents (wt%): (a) 2; (b) 5.

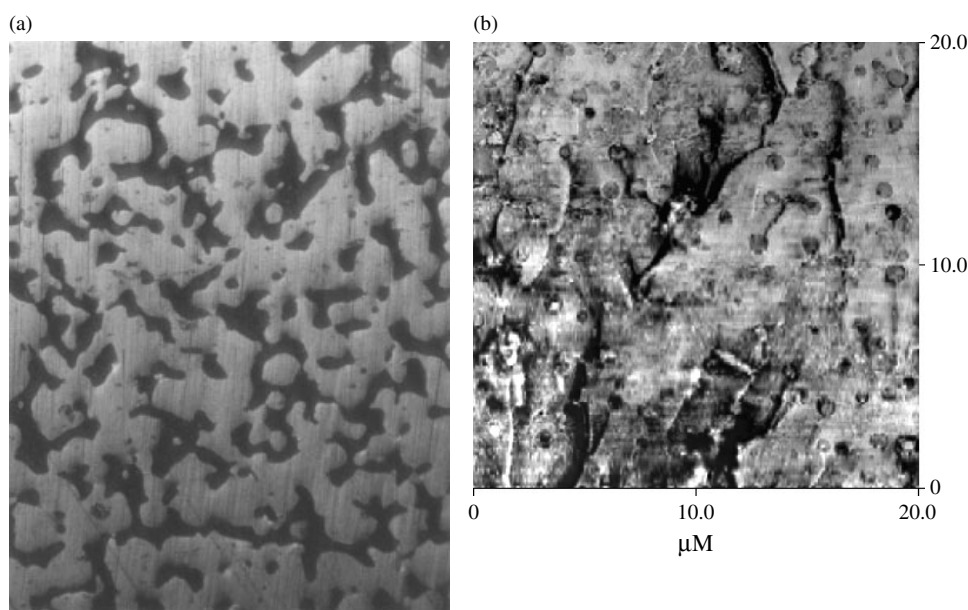


Figure 9. Microscope pictures for a ternary mixture containing 10 wt% phenoxy and 5 wt% PMMA: (a) OM; (b) AFM.

with the Fox equation,⁴⁴ could be related to some stoichiometric epoxy–amine imbalance during curing, possibly as a consequence of amine migration to the PMMA-rich regions.

Table 1 shows the variation of mechanical properties and fracture toughness for the addition of phenoxy to PMMA-modified epoxy mixtures. Although the stiffness of the PMMA-modified epoxy mixtures was

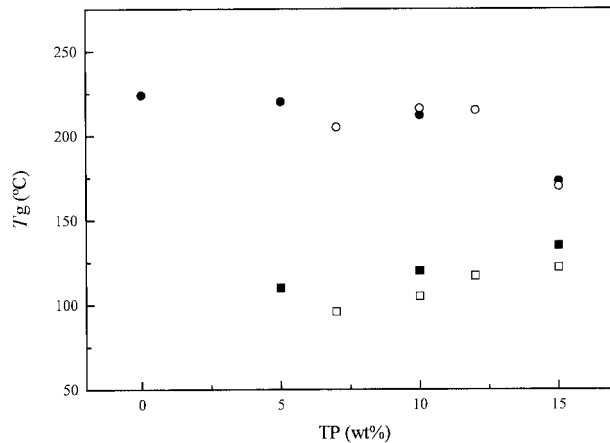


Figure 10. Glass transition temperatures of PMMA-modified mixtures for several phenoxy contents vs TP content for (O) epoxy-rich phase and (□) TP-rich phase. Closed symbols, PMMA as TP; open symbols, PMMA-phenoxy as TP.

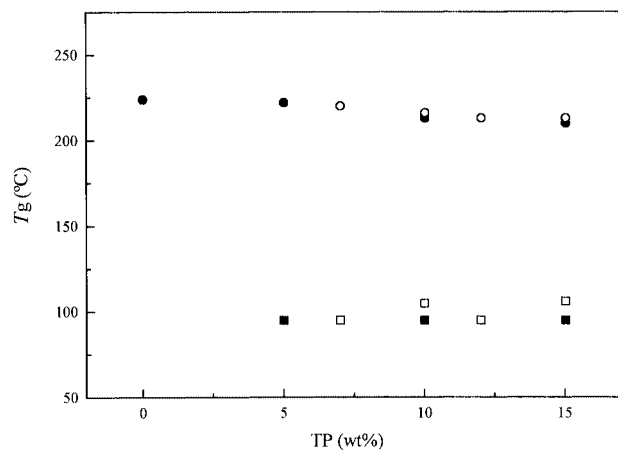


Figure 11. Glass transition temperatures of phenoxy-modified mixtures for several PMMA contents vs TP content for (O) epoxy-rich phase and (□) TP-rich phase. Closed symbols, phenoxy as TP; open symbols, phenoxy-PMMA as TP.

slightly higher than that of the neat epoxy matrix, its strength clearly decreased for non-particulate compositions. Otherwise, the fracture toughness clearly increased up to a 10 wt% PMMA content, subsequently reducing, possibly because the large epoxy-rich domains included in the narrow PMMA-rich phase were not able to stabilize the crack advance into the PMMA matrix, and also because of the above mentioned stoichiometric epoxy–amine imbalance during curing.

Phenoxy addition clearly enhanced the fracture behavior. Thus, on adding 2 or 5 wt% phenoxy to 5 wt% PMMA-modified mixtures, both particulate and some island-like microdomain-containing morphologies enhanced the small-strain properties and also increased nearly threefold the fracture toughness of the neat matrix. For the 10 wt% PMMA-modified mixture, as co-continuity also appeared with 2 wt% phenoxy addition, the fracture toughness was clearly enhanced. On the other hand, adding 5 wt% phenoxy also increased the strength with respect to that for the mixture without phenoxy. That modification led to a phase-inverted mixture and again the fracture toughness clearly decreased, but to a smaller extent than that for the 15 wt% PMMA-modified mixture.

Table 2 shows the variation in mechanical properties and fracture toughness for PMMA addition to phenoxy-modified epoxy mixtures. Once again, for the mixtures no containing PMMA, the existence of particulate morphologies enhanced the fracture toughness of these mixtures. The enhancement was higher, as were higher particle size and volume fraction. However, despite the experimental uncertainty, breakage of the 15 wt% phenoxy-modified mixture (which showed large islands of phenoxy-rich domains) occurred close to yielding but the fracture toughness was lower than those for the other phenoxy-modified mixtures.

Similar trends to those shown for phenoxy addition to PMMA-modified mixtures were observed for PMMA addition to the particulate phenoxy-modified mixtures as the morphologies evolved to co-continuity. Even for the epoxy mixture with a PMMA/phenoxy ratio of 5:10, no phase inversion was observed, possibly because of the lower molecular weight of phenoxy with respect to that for PMMA. These morphological changes slightly increased the

Table 2. Mechanical properties and fracture toughness of the ternary epoxy mixtures with phenoxy as the main thermoplastic

PMMA (%)	Phenoxy (%)	<i>E</i> (MPa)	Flexural strength (MPa)	<i>K</i> _{IC} (MPa m ^{1/2})	<i>G</i> _{IC} (J m ⁻²)	<i>T</i> _{g1} (°C)	<i>T</i> _{g2} (°C)
0	0	2580 ± 20	120 ± 1	0.80 ± 0.1	230 ± 30	—	224
0	5	2680 ± 40	125 ± 2	1.00 ± 0.06	320 ± 40	95	222
2	5	2745 ± 80	132 ± 4	1.28 ± 0.10	525 ± 50	95	220
5	5	3010 ± 35	123 ± 8	1.45 ± 0.12	615 ± 100	105	216
0	10	2515 ± 70	115 ± 5	1.34 ± 0.34	650 ± 315	95	213
2	10	2720 ± 35	121 ± 2	1.51 ± 0.10	735 ± 90	95	213
5	10	2810 ± 55	130 ± 3	1.70 ± 0.13	905 ± 135	106	213
0	15	2790 ± 25	130 ± 2	1.03 ± 0.08	335 ± 50	95	210

small-strain mechanical properties and also the fracture toughness of the mixtures. Hence, in the case of epoxy modification with two miscible thermoplastics with such similar glass transition temperatures as PMMA and phenoxy, the morphological features, and consequently the ultimate behavior, seem to be related to the overall amount of thermoplastic contained in the mixture. However, factors such as the molecular weight of each thermoplastic, and also the extent of miscibility between the separated phases, can lead to small morphological and thermal variations for the same overall content of thermoplastic as their relative ratio changes. Thereby, in ternary mixtures of thermosetting resins with two thermoplastics, greater effort becomes necessary to understand the morphological generation, and thus the ultimate properties.

CONCLUSIONS

The morphology and ultimate properties in cured reactive ternary blends containing two thermoplastics predissolved in a thermoset DGEBA–DDS epoxy resin were investigated. The thermoplastics used, PMMA and phenoxy, are miscible together and they phase-separate from the epoxy resin at closer curing times. Modified mixtures with each thermoplastic were heterogeneous, their morphologies being dependent on the content of thermoplastic. Optical microscopy, atomic force microscopy and dynamic mechanical analysis were used to study the heterogeneity level on the cured epoxy mixtures. It was shown that the analysis of the variation of loss modulus with temperature, together with that for storage modulus, is an excellent approach for controlling the extent of phase separation in the final mixtures.

The addition of small amounts of the second thermoplastic modified the final morphologies from particulated to co-continuous and from this latter type to phase inverted microstructures. Phase inversion may occur for overall TP contents ≥ 15 wt% as PMMA or phenoxy is the main TP in the mixture. The developed morphologies were as simple as when only one thermoplastic was used for modification, although small differences were observed as a function of the molecular weight of the second thermoplastic added. Thus, the control of morphological evolution becomes very simple. However, more work has to be done concerning the thermodynamics of phase separation during curing in order to gain further understanding of the mechanism for inducing heterogeneities.

For particulated or co-continuous morphologies, with the exception of mixtures in which PMMA was the main TP used, the strength fell as co-continuity occurred, and both flexural modulus and strength varied within a narrow range. A significant increase in fracture toughness was observed especially for the mixtures with some level of co-continuity. Phase inversion led to poor strength and also fracture toughness, surely as a consequence of the brittleness of the thermoplastics used.

Currently, modification of several thermosetting resins with different modifier mixtures is being investigated in our laboratories by analyzing the influence of their molecular weights and also considering the morphological variations occurring as the curing agent is changed.

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