Morphology profiles obtained by reaction-induced phase separation in epoxy/polysulfone/poly(ether imide) systems

MI Giannotti,[1] I Mondragon,[2] MJ Galante[1] and PA Oyanguren[1]*

[1]*Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), JB Justo 4302, 7600 Mar del Plata, Argentina*

[2]*'Materials + Technologies' Group, Escuela Ingeniería Técnica Industrial, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda Felipe IV, 1 B 20011 San Sebastián — Donostia, Spain*

Abstract: The reaction-induced phase separation in epoxy/aromatic diamine formulations simultaneously modified with two immiscible thermoplastics (TPs), poly(ether imide) (PEI) and polysulfone (PSF), has been studied. The epoxy monomer was based on the diglycidyl ether of bisphenol A (DGEBA) and the aromatic diamine was 4,4′-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA). Phase-separation conversions are reported for various PSF/PEI proportions for blends containing 10 wt% total TP. On the basis of phase-separation results, a conversion–composition phase diagram at 200 °C was compiled. This diagram was used to design particular cure cycles in order to generate different morphologies during the phase-separation process. It was found that, depending on the PSF/PEI ratio employed, a particulate or a morphology characterized by a distribution of irregular PEI-rich domains dispersed in an epoxy-rich phase was obtained for initially miscible blends. Scanning electron microscopy (SEM) characterization revealed that the PEI-rich phase exhibits a phase-inverted structure and the epoxy-rich matrix presents a bimodal size distribution of TP-rich particles. For PSF/PEI ratios near the miscibility limit, slight temperature change result in morphology profiles.
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INTRODUCTION

The field of thermoset/thermoplastic blends has received considerable attention during the past decade.[1] Most of these blends are prepared starting from a homogeneous solution of the thermoplastic polymer in the thermoset precursors by inducing phase separation during the thermoset polymerization.[2] A new material is generated with distinct properties with respect to those of the individual polymers.

One of the advantages of using the reaction-induced phase-separation process to generate modified thermosets is that, by an adequate selection of cure cycles and initial formulations, parts exhibiting positionally different morphologies can be obtained. Sandwich structures consisting of phase-separated surface layers (opaque) and a homogeneous core (transparent) were obtained when epoxy resins were modified with castor oil.[3] More recently, Stefani *et al.*[4] showed that a poly(methyl methacrylate) (PMMA)-modified epoxy-amine system cured in a heated mould could give morphology gradients with various optical properties depending on the selected cure cycle.

An interesting possibility is the simultaneous addition of two polymers to the thermosetting resin before curing. To our knowledge, only a few studies of ternary blends involving a thermoset precursor and two linear polymers have been reported.[5–8] Recently, we have studied the reaction-induced phase separation taking place in a reactive epoxy solvent modified simultaneously with two thermoplastic (TP) polymers: poly(ether imide) (PEI) and polysulfone (PSF).[9,10] The selected TPs have different phase behaviour with temperature in epoxy/TP mixtures: epoxy/PEI blends showed an upper critical solution temperature (UCST) behaviour, while epoxy/PSF mixtures were of the lower critical solution temperature (LCST) type. On the other hand, PEI/PSF were completely

immiscible between them. In the epoxy/PSF/PEI blends we observed that miscibility increased with temperature, which implies UCST behaviour. The increase in the TP concentration in the blends led to an increase in the temperature required to generate a homogeneous solution. Furthermore, we determined that these curves are not symmetric, and that small additions of PEI to epoxy/PSF blends provoked a steeper increase of the cloud point temperature than in the other case.

Conversion–composition phase diagrams at constant temperature were also generated for various cure agents and total TP content.[9] Two phase-separation processes during the course of the polymerization reaction were observed in initially homogeneous blends. These diagrams were used to analyse the implications on morphologies and associated properties of the resulting materials, with appropriate pre-curing and post-curing schedules and PSF/PEI ratios.[10]

Our recent study confirmed that, depending on the miscibility of the initial system, particulate or double-phase morphology is obtained for blends located outside or inside the immiscibility window, respectively.

The present study was intended to obtain materials with morphology profiles by phase separation during polymerization of initial mixtures composed of a reactive polymer precursor modified with PSF/PEI proportions located near the miscibility limit. The effects of important parameters such as cure temperature and blends composition, on the process were investigated in detail.

EXPERIMENTAL

The chemical structures of the monomer and the TPs are indicated in Fig 1. The epoxy resin used in this work was a diglycidyl ether of bisphenol A (DGEBA) (Dow DER 332), with $n = 0.03$. Two amorphous TPs were used as modifiers for the epoxy resin: polysulfone (PSF) (Amoco Chemicals Udel P1700) with a glass transition temperature T_g of 190 °C and poly(ether imide) (PEI) (General Electric Ultem 1000) with a T_g of 225 °C. They were used as received. The reported values of number-average and weight-average molecular weights for PEI were, respectively, $M_n = 26\,000$ and $M_w = 50\,000\,\mathrm{g\,mol^{-1}}$.[11] The PSF data were $M_n = 38\,000$ and $M_w = 63\,000\,\mathrm{g\,mol^{-1}}$.[12] The epoxy resin and its blends were cured with the aromatic diamine 4,4′-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA) (Lonza). The hardener was used at a stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1.

Modified epoxy resins containing 10 wt% of TP were prepared using a standard procedure. The TP were dissolved in dichloromethane (CH$_2$Cl$_2$) and mixed with the resin at room temperature. Most of the solvent was evaporated at room temperature and the residual amount was eliminated by heating at 80 °C
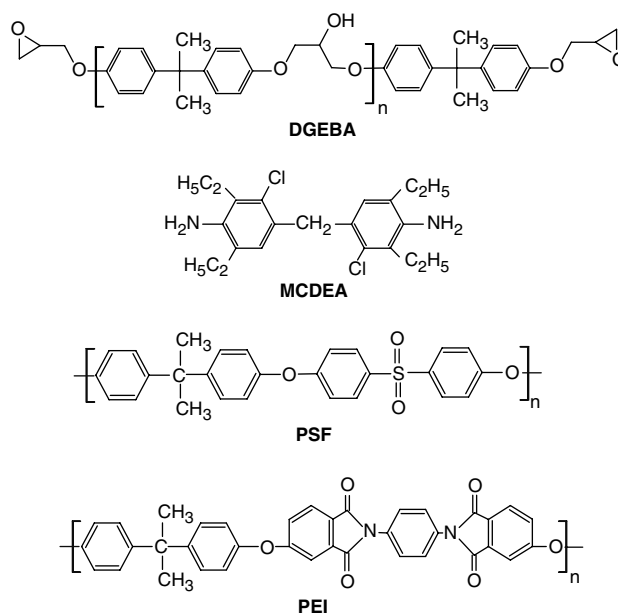

Figure 1. Chemical structures of the epoxy monomer diglycidyl ether of bisphenol A (DGEBA), the amine 4,4′-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA), and the thermoplastics polysulfone (PSF) and poly(ether imide) (PEI).

for 24 h. In a second step, a stoichiometric amount of the aromatic diamine MCDEA was dissolved at 90 °C.

Cloud-point and secondary phase-separation measurements in reactive mixtures, containing different PSF/PEI relations, were determined using an Olympus BH-2 optical microscope equipped with a Mettler EP82HF heating stage. One drop of the mixture was placed between a glass microscope slide and a cover slip separated by a spacer of 1 mm thickness, and this was inserted into the heating stage programmed at constant temperature. The cloud-point and secondary phase-separation times, t_{cp} and t_{ps}, were determined as the onset times at which a decrease in the transmitted light intensity was recorded. Both t_{cp} and t_{ps} were expressed as the corresponding conversion values, x_{cp} and x_{ps}, using the polymerization kinetics determined in previous work.[9]

Plates of 2 mm thickness were prepared using a glass mould coated with Frekote 44 releasing agent. The cure was carried out in an oven at various curing temperatures (180, 200 and 220 °C) with degassing for the first 30 min.

Chemical resistance was evaluated by immersing the samples in dichloromethane.

Specimens fractured at room temperature, coated with a fine gold layer, were observed by scanning electron microscopy (SEM), using a Jeol JXA-8600.

RESULTS AND DISCUSSION

As we discussed in previous work,[9] the increase in the total TP proportion up to 10 wt% provokes the appearance of an immiscibility window in these blends. Because of that, mixtures that are homogeneous at the beginning of the curing reaction at the selected
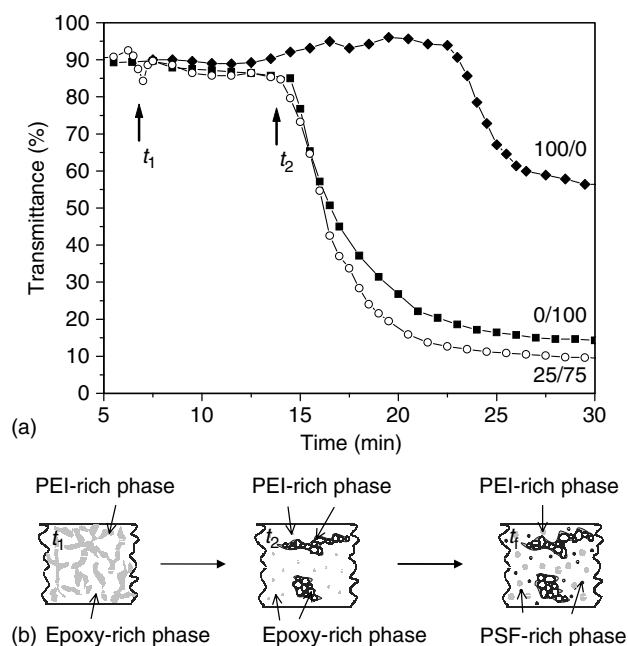
Figure 2. (a) Intensity of the transmitted light as a function of polymerization time at 200 °C for blends containing 10 wt% total TP, prepared with various PSF/PEI ratios: 100/0, 0/100 and 25/75. The arrows indicate the onset of the phase-separation process.
(b) Evolution of the morphology is illustrated for the 25/75 blend as a function of reaction time, where t_f is the time at which the final morphology is attained.

temperature are limited to a narrow PSF/PEI range of compositions. The initial heterogeneous blend compositions were in the range 30–97 wt% PSF at 200 °C. Figure 2(a) shows the experimental curves of the intensity of transmitted light as a function of polymerization time for blends prepared with PSF/PEI ratios of 100/0, 0/100 and 25/75 when cured at 200 °C. The composition of the ternary blend was selected in a manner that it was initially homogeneous and was located near the immiscibility window at the cure temperature employed. The binary blends' behaviour shows that PSF phase-separates at higher conversions than PEI, and close to gelation, reflecting the higher solubility of PSF in the epoxy matrix at 200 °C. The generation of a PEI-rich phase leads to a sharp decrease in transmitted light intensity while the segregation of a PSF-rich phase is difficult to determine precisely because of the smooth decrease in the transmitted light intensity. This could be a consequence of the similar refractive indices of the two phases and/or the small size of the generated particles, which explains the translucent aspect of PSF-cured blends.

Concerning the ternary blend, a double phase separation was observed. The relative magnitude of the steps in transmission was related to the composition of the phases at the phase-separation time. At $t = t_1$ the first phase-separation process involved the generation of two phases, one rich in epoxy-amine and the other rich in PEI. The small difference in composition, and thus in refractive indices of the phases, led to a smooth change in transmitted light intensity. The demixing system was then characterized by a

certain level of interconnectivity in both the minor and the major phases. A representation of the phase-separation process is schematically shown in Fig 2(b). The evolution of species through the continuation of the polymerization provoked the secondary phase separations that took place in both phases. At $t = t_2$ a secondary phase separation occurred, leading to a sharp decrease in the intensity of transmitted light. At this time, the phase separation of the PEI dissolved in the epoxy-rich phase generated a dispersion of PEI-rich particles in an epoxy-rich matrix. Although no change in transmittance was detected, coarsened PEI-rich dispersed domains suffered secondary phase separation. The dispersed phase inside the PEI domains was formed of epoxy-amine polymer. The t_2 transition was neat and was related to a change from an opalescent to an opaque state. Consequently, while the reaction proceeded the generation of the PSF-rich phase could not be detected. The PEI secondary phase separation occurred at a lower conversion, which meant a less viscous system and a faster transfer of monomers (and epoxy-amine species) between the epoxy-rich and PEI-rich phases than in the case of PSF. Small PSF particles were formed due to their phase separation taking place near gelation. Then, as consequence of the different miscibility of both TPs, bimodal particle-size distribution was generated where large particles belonged to PEI and small ones were PSF, as was demonstrated in previous studies.[9,10]

Figure 3 shows the phase-separation conversion x_{ps} *versus* composition phase diagram for blends containing 10 wt% total TP and cured at 200 °C, presented as a function of the relative contribution of PSF to the total TP content. Blends with a concentration of PSF higher than 30 wt% were initially immiscible.[9] It can be observed that the first phase-separation conversion curve represented by the cloud-point curve (CPC) showed a constant decrease with the addition of PSF. On the contrary, the PSF and PEI secondary phase separations would take place
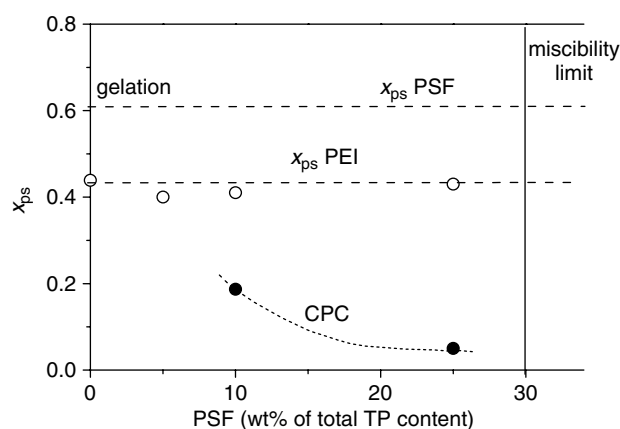

Figure 3. Phase diagram showing conversion as a function of the relative fraction of PSF of blends containing 10 wt% total TP and cured at 200 °C. The experimental cloud-point curve (CPC, black circles) and the secondary phase separation of PEI (white circles) are shown, together with the gel conversion of the thermoset. It was assumed that PSF phase-separates at gelation.

at conversions similar to those corresponding to the binary systems.

The final morphologies obtained for blends prepared with various PSF/PEI ratios are shown in Figs 4 and 5. The bright domains correspond to the TP-rich phase (the SEM technique can not distinguish between PEI and PSF) while the dark ones to the epoxy-rich phase. The micrographs obtained for PSF/PEI proportions up to 15/85 were not significantly different (Fig 4). As expected, bimodal particle-size distributions were obtained for all the blends analysed, except for PSF/PEI = 5/95. In this case, the PSF-rich domains generated could have been too small to be seen. Figure 5 shows the morphologies observed when the PSF concentration increased. The volume fraction of the PEI-rich dispersed domains, generated as result of the first phase-separation process, increased gradually while the PSF content in the formulation increased. No evidence of the presence of these domains was seen by monitoring all the sample surfaces for low PSF content formulations. Blends with PSF/PEI = 20/80 showed small PEI-rich dispersed domains in the epoxy-rich matrix [Fig 5(a)].

As expected, an enlargement of the epoxy-rich matrix showed a bimodal particle-size distribution [Fig 5(b)]. However, blends containing a higher PSF content exhibited co-continuous morphology [Figs 5(c) and (d)]. The SEM micrographs obtained at various magnifications revealed that the PEI-rich phase exhibited a phase-inverted structure and the epoxy-rich matrix presented a bimodal dispersion of TP-rich particles.

Formulations with PSF/PEI ratios near the miscibility limit phase-separated at lower conversion levels, ie shorter cure times (see Fig 3). In the case of PSF/PEI = 25/75, the cloud-point time was $t_{cp} = 5$ min. It was thus expected that small temperature changes over the course of phase separation would have an appreciable influence on the subsequent phase-separation behaviour. In other words, different domain structures could be produced at the same final temperature depending on the previous thermal history. Figure 6 shows the domain structure obtained after a formulation with PSF/PEI = 25/75 at various temperatures. The micrographs for samples cured at 200 °C and 220 °C are the result of
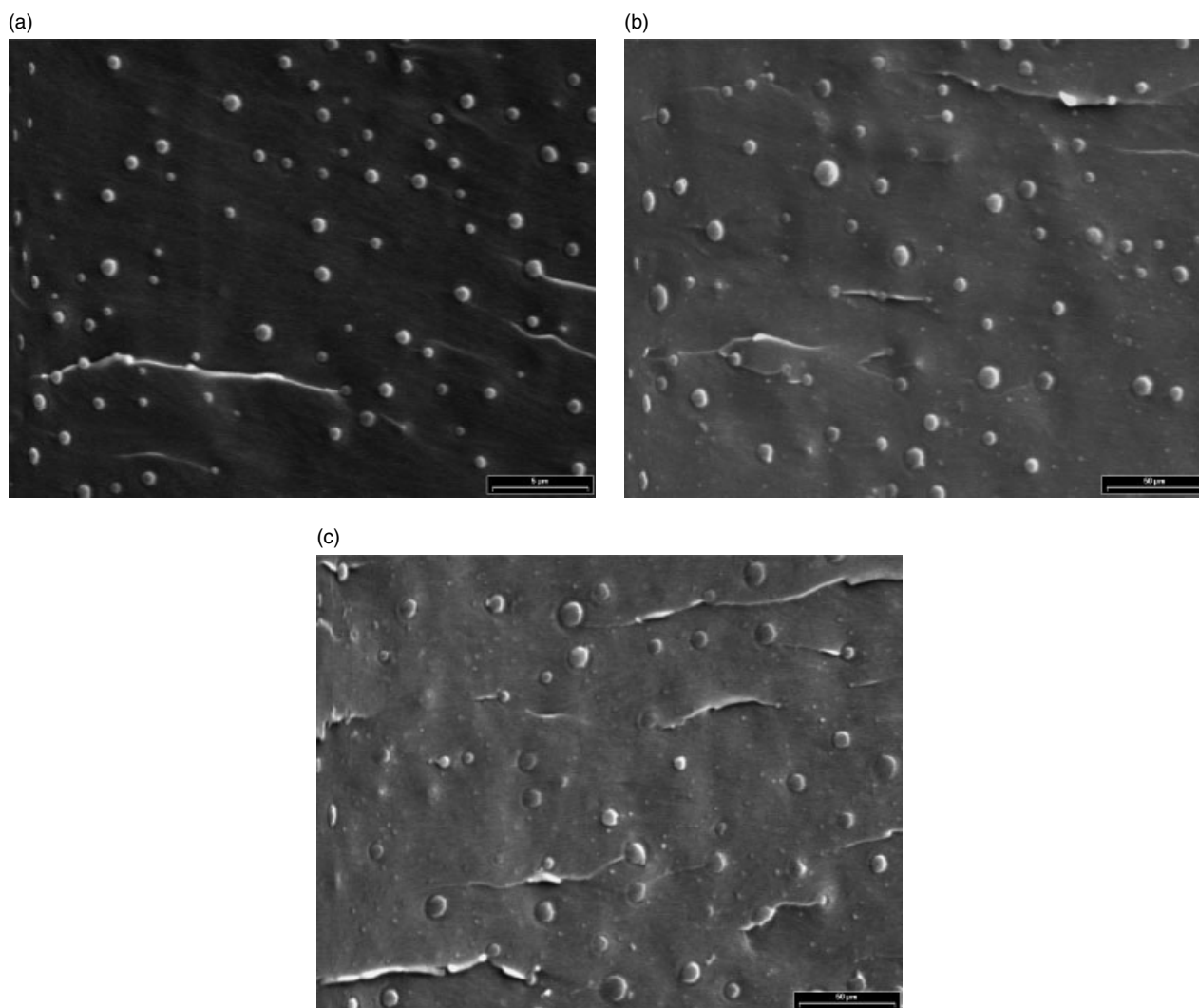

Figure 4. SEM micrographs of blends containing 10 wt% total TP cured at 200 °C, showing the morphologies obtained depending on the PSF/PEI ratio: (a) 5/95; (b) 10/90; (c) 15/85.
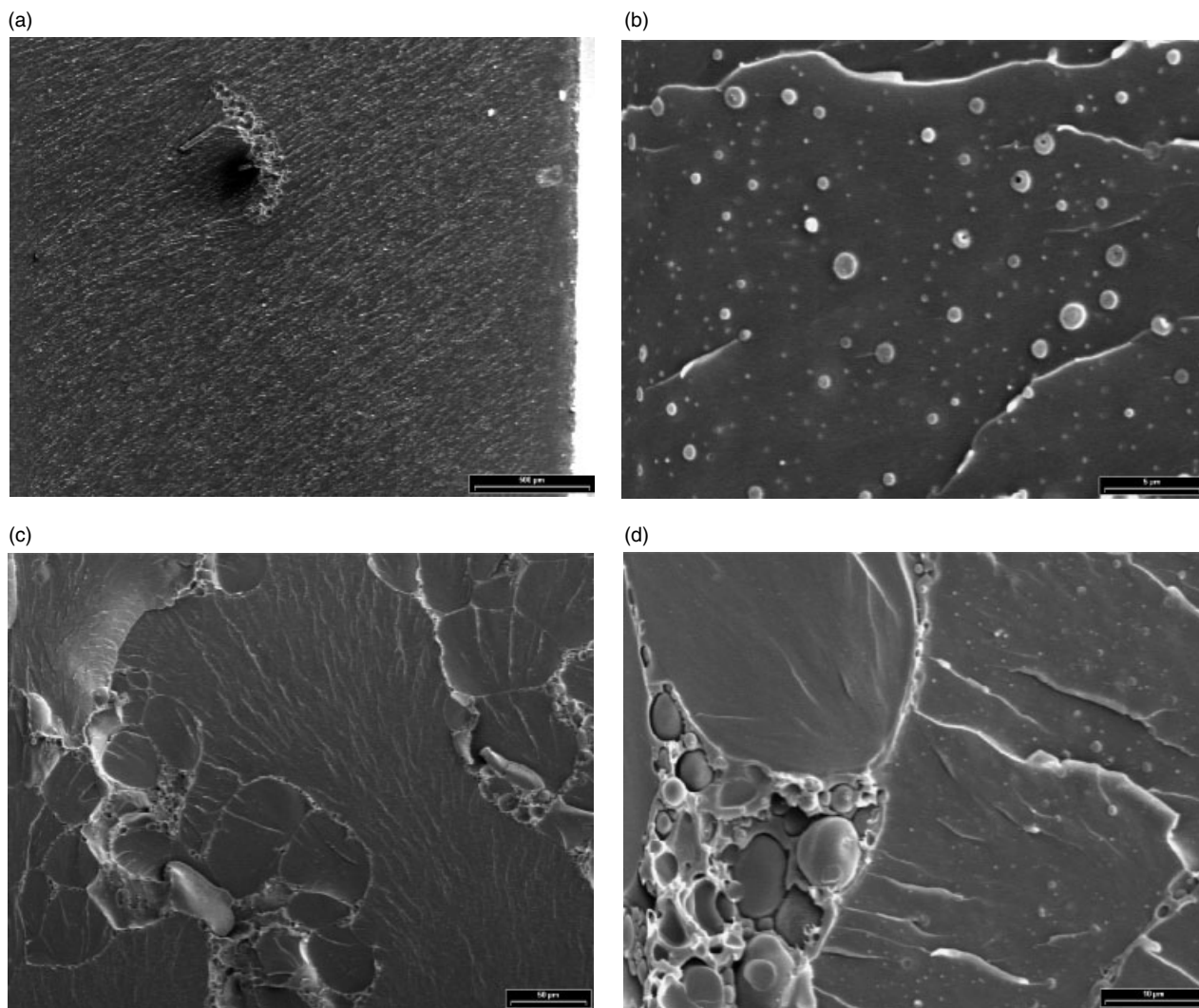
(a)

(b)

(c)

(d)

Figure 5. SEM micrographs of blends containing 10 wt% total TP cured at 200 °C, showing the morphologies obtained depending on the PSF/PEI ratio: (a) 20/80, low magnification; (b) 20/80, high magnification; (c) 25/75, low magnification; (d) 25/75, high magnification.

phase separation starting from a homogeneous solution. When comparing Figs 6(b) and (c), two factors have to be considered. Firstly, the system was characterized by UCST behaviour,[9] ie miscibility increased with temperature. The volume fraction of the PEI-rich phase (first phase-separation process) thus increased as the cure temperature decreased [Fig 6(b)]. Secondly, the cure temperature affected the final morphology by determining the viscosity of the reaction medium. Curing at higher temperatures resulted in a more pronounced interruption of the phase connectivity [Fig 6(c)]. A noticeable morphological change from co-continuous domains [Fig 6(b)] to a double-phase morphology [Fig 6(c)], where PEI-rich circular-shaped islands were dispersed in an epoxy-rich matrix, was developed by increasing the cure temperature.

The blend cured at 180 °C showed a morphology gradient where borders of approximately 300 µm thick surrounded a 1.6 mm thick core [Fig 6(a)]. As shown in Fig 7, a closer inspection reveals the morphology profiles generated during polymerization leading to a sandwich structure. The border's morphology consisted of a random distribution of

spherical particles [Figs 7(a) and (b)], while the core showed a co-continuous morphology [Fig 7(c)] resembling the structures obtained when curing at higher temperatures [see Figs 5(c) and (d)]. A possible explanation for the complex morphology obtained is that the initial mixture of components was heterogeneous. The cure temperature decrease along with the temperature profiles generated inside the sample contributed to the formation of two phases, one of them rich in epoxy and the other rich in PEI. The initial mixture next to the mould walls probably remained homogeneous because thermal equilibrium was reached. In contrast, a slight temperature decrease along the centre of the mould provoked a PEI-rich phase separation before any reaction had taken place.

All the samples analysed exhibited excellent chemical resistance to solvents. No shape changes were observed after 48 h of immersion in dichloromethane, even for the sandwich structure plate. However, when this last sample was deliberately broken, disintegration of the core occurred. This phenomenon may have been related to the co-continuous morphology
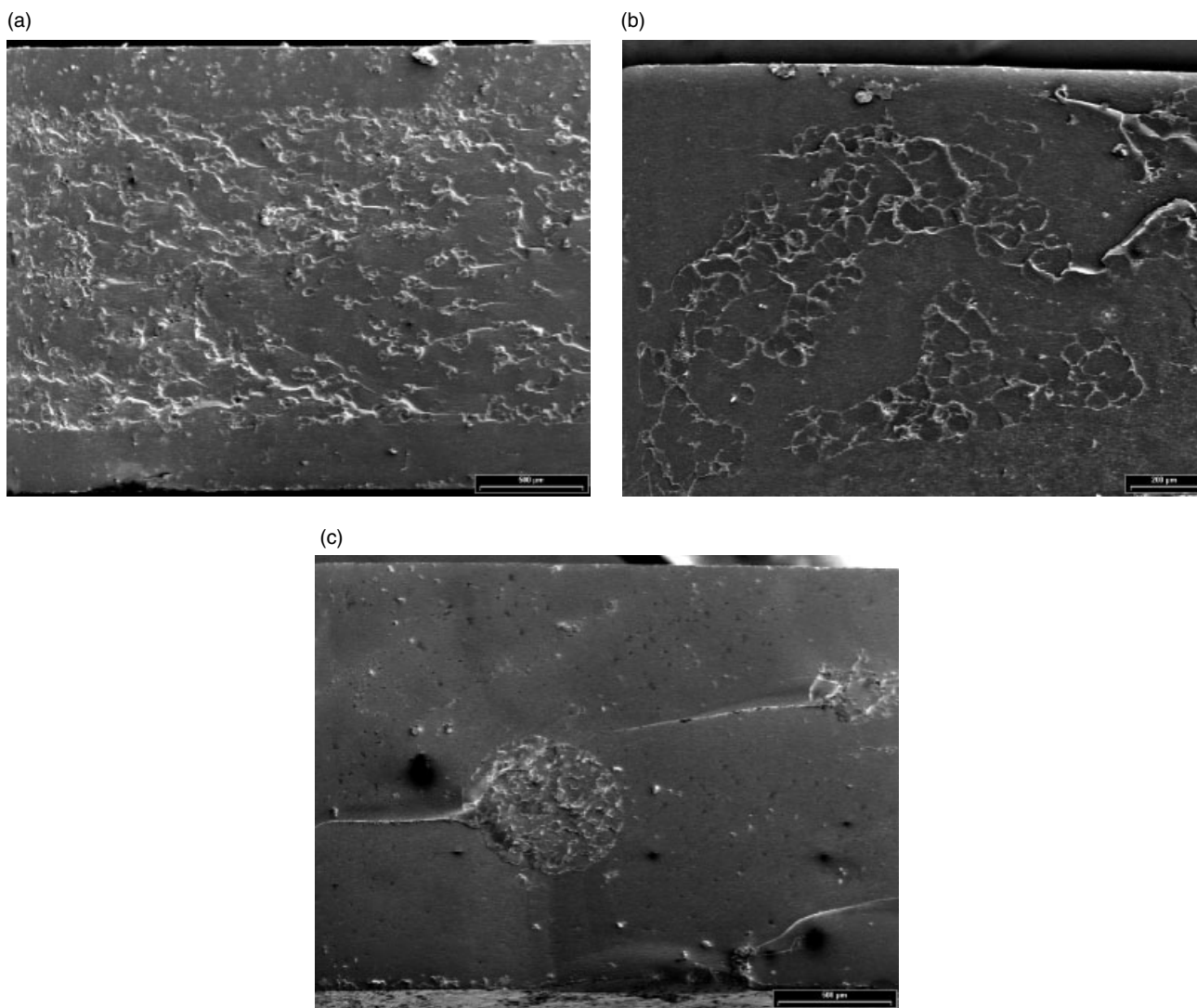
(a)

(b)

(c)

Figure 6. SEM micrographs of blends containing 10 wt% total TP with PSF/PEI = 25/75 ratio, cured at different temperatures: a) 180 °C; b) 200 °C; c) 220 °C.

developed. Owing to the fact that the morphology of the borders are completely different, they remained intact.

CONCLUSIONS

The reaction-induced phase separation taking place in a reactive epoxy solvent modified simultaneously with PSF and PEI was studied. Experimental observations revealed the existence of multiple phase separation. The first phase-separation conversion represented by the cloud-point curve showed a constant decrease with the addition of PSF, while second phase separations occurred at similar to the binary system conversion values. The other TP, PSF, phase-separated at conversions near gelation.

On the basis of the phase-separation results, a conversion–composition phase diagram at 200 °C was compiled. This diagram was used to design particular cure cycles to generate different morphologies during the phase-separation process. It was found, that depending on the PSF/PEI ratio

employed, a particulate or a completely different morphology, characterized by a distribution of irregular PEI-rich domains dispersed in an epoxy-rich phase, was obtained when curing initially miscible blends. SEM characterization revealed that the PEI-rich phase had a phase-inverted structure and the epoxy-rich matrix presented a dispersion of TP-rich particles with a bimodal particle-size distribution.

For PSF/PEI ratios near the miscibility limit, slight temperature profiles resulted in morphology gradients. In terms of practical applications, these experimental results provide new insight into manufacturing polymeric materials with variable gradients of structure, and thus gradients of properties.