The role of partial miscibility on the properties of blends of a polyetherimide and two liquid crystalline polymers*

S. S. Bafna, T. Sun and D. G. Baird†
Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0211, USA

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This paper is concerned with the existence of partial miscibility of a polyetherimide (PEI) with both amorphous and semicrystalline liquid crystalline polymers (LCPs) and its effect on the morphology of the blends of these polymers. Partial miscibility was determined by measuring the shift in the glass transition temperatures as determined by dynamic mechanical thermal analysis and differential scanning calorimetry. With increasing concentration of the LCP in the PEI/LCP blends, the glass transition temperature of the PEI phase shifted to a lower temperature. Annealing and mixing history were also observed to affect the degree of shift in the glass transition temperature. Morphologies of the partially miscible systems were found to be quite different from those of an immiscible system. It is likely that due to partial miscibility in these blends, a PEI-LCP solid solution coexists with the neat LCP phase.

(Keywords: miscibility; polyetherimide; liquid crystalline polymer; blends; *in situ* composite)

INTRODUCTION

Interest in *in situ* composites based on blending liquid crystalline polymers (LCPs) with engineering thermoplastics has grown in recent years primarily due to the possibility of their having a variety of processing options and relatively high mechanical performance[1–9]. It is well known that the maximum enhancement in mechanical properties of short fibre composites can be achieved by using very fine fibres with a large aspect ratio and by promoting strong interfacial adhesion between the fibres and the polymeric matrix[10]. As pointed out by Baird *et al.*, the morphology and properties of *in situ* composites should be affected by the interaction between the LCP and the matrix[11]. Factors such as miscibility or compatibility could contribute significantly to the interaction between the matrix and the LCP and hence to the physical properties of *in situ* composites.

Studies dealing with the miscibility of blends of a thermotropic liquid crystalline copolymer consisting of ethylene terephthalate and *p*-hydroxybenzoic (PET/PHB) with various thermoplastics can be found in the literature[12–15]. The effects of miscibility of the matrix and reinforcing phase on the development of *in situ* composites have been studied by Zhuang *et al.*[14]. Polystyrene (PS), poly(ethylene terephthalate) (PET) and polycarbonate (PC) were used as the matrices and PET/60PHB (60 denotes the mole per cent of PHB in the copolyester) as the reinforcing phase. Blends were prepared by both solution and melt blending. On the basis of the results from differential scanning calorimetry (d.s.c.), scanning electron microscopy (SEM), and dielectric thermal analysis (d.e.t.a.), the authors concluded that PS was immiscible, whereas both PC and PET were partially miscible with PET/60PHB, PET being miscible to a higher degree than PC. The glass transition corresponding to the thermoplastic phase did not shift for PS upon blending with the LCP. There was a small but significant decrease in the glass transition temperature, T_g, upon blending with PC and the shift was detectable across the entire composition range for PET blends. The presence of ellipsoidal LCP particles and microfibrils was observed. However, little attempt was made to explain the reason for the observed morphology or correlate it with miscibility. Recently, it has been found that a single phase can be prepared with PET/60PHB and PC through solvent casting[15]. The blends of PET/60PHB with PC were originally reported to be only partially miscible[14]. However, they phase separate upon heating.

Polyetherimide (PEI), an amorphous polymer commercially known as Ultem, has been blended with LCPs to prepare high modulus *in situ* composites[4,16–18]. It has been reported that Ultem is miscible with polybenzimidazole (PBI) [19] and poly(ether ether ketone) (PEEK)[20,21]. Recently the miscibility between Ultem and LCPs and its effect on the morphology and mechanical properties of Ultem/LCP *in situ* composites were studied in our laboratory[17]. It has been found that Ultem is immiscible with Vectra A900 (a liquid crystalline aromatic copolyester consisting of 73% hydroxybenzoic acid and 27% 2-hydroxy 6-naphthoic acid moieties), but partially miscible with Granlar (a liquid crystalline aromatic copolyester consisting of terephthalic acid, phenyl-hydroquinone and phenyl-ethyl hydroquinone)[18]. As revealed by dynamic mechanical thermal anaysis (d.m.t.a.), the mixing of the latter can be improved by increasing the

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† To whom correspondence should be addressed

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number of passes through an extruder. The flexural and tensile moduli of the *in situ* composites based on these two blend systems have also been determined as a function of the blend composition. The modulus deviation from the rule of mixtures was interpreted in terms of differences in miscibility and hence differences in the interfacial adhesion between components for these two blend systems.

In this paper the existence of partial miscibility of Ultem with both an amorphous and a semicrystalline LCP and its effect on the morphology of the *in situ* composites based on these blends are studied. The effects of the annealing and mixing history on partial miscibility and phase dispersion are also discussed.

EXPERIMENTAL

Materials and sample preparation

The amorphous matrix polymer used was a PEI (Ultem 1000) made by General Electric. Two LCPs (HX1000 and HX4000) made by DuPont were used in this study. HX4000 is a semicrystalline copolyester while HX1000 is an amorphous copolyester. The exact compositions of these copolyesters is proprietary DuPont information.

Pellets of Ultem were dried at 170°C. Pellets of the LCPs, HX1000 and HX4000, were dried at 150°C. All drying processes were carried out in a vacuum oven for at least 24 h. The dried pellets were then tumbled in predetermined weight ratios. A laboratory single screw extruder (Killion KL100) connected to a 102 mm wide sheet die was used to generate the sheets. Rectangular plaques measuring approximately 75 mm × 85 mm × 1.75 mm were moulded using an Arburg (221-55-250 Allrounder) injection moulding unit. Temperatures were set at 300, 355 and 360°C in zones 1, 2, and 3 of the barrel, respectively, and at 360°C in the nozzle. The mould temperature was set at 150°C.

To study the effect of mixing history, pellets of Ultem and the LCP were mixed together and extruded in a single or a twin screw extruder connected to a pelletizing die. The extrudate was quenched in ice water and continuously pelletized. In order to impart additional mixing history, the pellets were re-extruded in the single screw extruder and then pelletized again. The blended pellets were then used to make moulded plaques.

Dynamic mechanical tests

Dynamic mechanical tests on the injection moulded plaques were carried out in the torsional mode using a Rheometrics Mechanical Spectrometer (RMS 800). Rectangular samples with dimensions of 45 mm × 12.5 mm were cut from the injection moulded plaques. The loss tangent ($\tan\delta$) of the samples was monitored and recorded as a function of temperature. The frequency of oscillation was 10 rad s^{-1} and the strain was 0.05%. The experimental temperature was raised stepwise at a rate of 5°C min^{-1} until the modulus of a given sample dropped appreciably. It should be noted that the various figures (*Figures 1*, *3*, *8*, *9* and *10*) only show a few representative data points (approximately 25°C apart) so that the figures remain uncluttered and easily legible. However, this must not be misinterpreted to imply that the experimental data points were measured 25°C apart (they were measured at intervals of 5°C).

Thermal analysis

A Seiko 1 DSC (Model 210) was utilized for the thermal analysis of these blends. The heating rate was fixed at 10°C min^{-1} for all the samples and prepurified nitrogen was used as the purge gas.

Morphology

The morphology of the blends was determined by SEM using a Cambridge Stereoscan S200 with an accelerating voltage of 25 kV. The samples were fractured perpendicular or parallel to the main flow direction after immersing them in liquid nitrogen. The fractured surfaces were sputter coated with gold to provide enhanced conductivity.

RESULTS AND DISCUSSION

To study the miscibility of the Ultem/HX4000 and Ultem/HX1000 blends, their T_gs were measured as a function of the blend composition using d.m.t.a. and d.s.c. The dynamic torsion test results for the Ultem/HX4000 system are shown in *Figure 1*. The T_gs of Ultem and HX4000 were found to be 228°C and 183°C, respectively. With increasing concentration levels of HX4000 in the injection moulded Ultem/HX4000 composites, the T_g of the Ultem phase shifts to a lower temperature, and the peak height of the loss tangent ($\tan\delta$) *versus* temperature curve decreases. Meanwhile, a shoulder which characterizes the segmental motion of HX4000 can be observed for all the blend compositions studied. The shift in T_g suggests that HX4000 is partially miscible with Ultem. It seems there are two phases existing in the composite: a pure HX4000 phase and a phase rich in Ultem with some HX4000 dissolved in it. The latter phase presents a lower T_g than that of neat Ultem and may give a higher matrix/fibril interaction in the (Ultem-HX4000)/HX4000 system.

To confirm the results obtained from d.m.t.a., d.s.c. thermograms of the Ultem/HX4000 composites at various blend compositions were also studied (*Figure 2*). With increasing content of HX4000 in the blends, the T_g of the Ultem-rich phase also shifts to a lower temperature. This again suggests that Ultem and HX4000 are partially

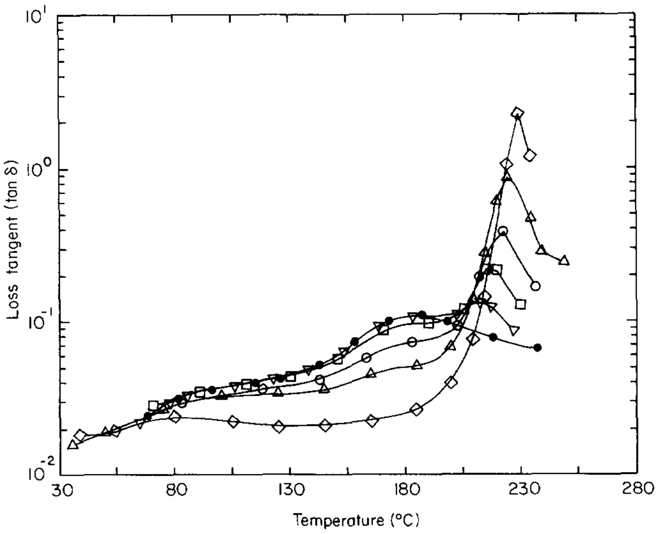

Figure 1 Loss tangent ($\tan\delta$) *versus* temperature for Ultem/HX4000 blends with various composition ratios: ◇, 100/0; △, 70/30; ○, 50/50; □, 30/70; ▽, 10/90; ●, 0/100

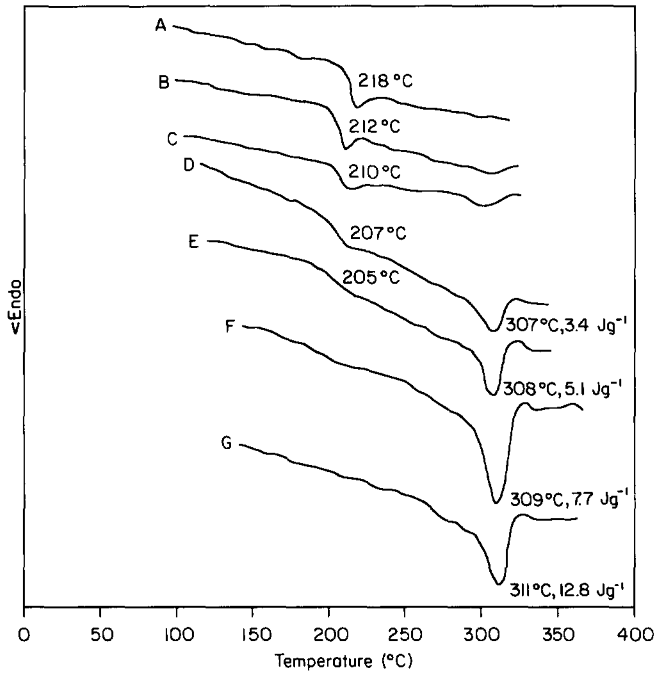

Figure 2 D.s.c. thermograms of Ultem/HX4000 blends with various composition ratios: A, 100/0; B, 80/20; C, 70/30; D, 50/50; E, 30/70; F, 10/90; G, 0/100

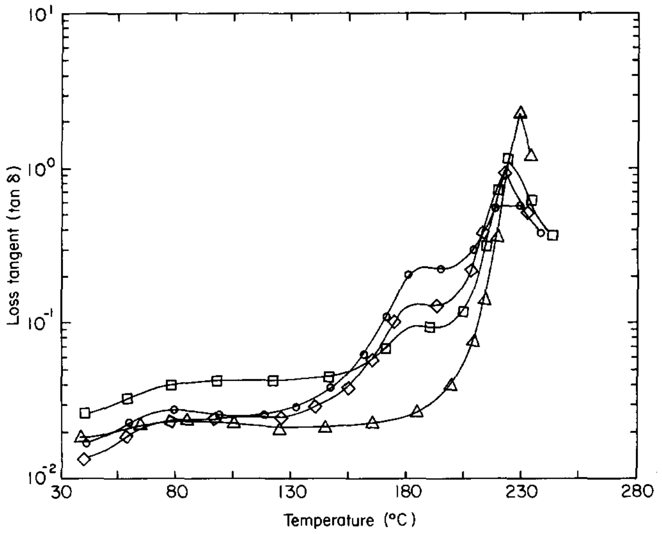

Figure 3 Loss tangent (tan δ) *versus* temperature for Ultem/HX1000 blends with various composition ratios: △, 100/0; □, 70/30; ◇, 50/50; ○, 30/70

miscible. The observed endothermic peak is caused by the melting of HX4000 crystallites in the blends. In the case of the Ultem/HX1000 blends, two T_gs can also be observed (*Figure 3*). The lower one (at 185°C), characterizing the T_g of HX1000, remains almost unchanged as the blend composition is varied. But the higher one (i.e. the T_g of the Ultem-rich phase) decreases as the concentration level of HX1000 is increased. The d.s.c. thermograms of the Ultem/HX1000 blends show similar trends (*Figure 4*). The T_g, as determined by d.s.c., of the Ultem phase in the blends dropped to 212°C as compared with 218°C for neat Ultem. The fact that no endothermic melting peak can be detected in Ultem/HX1000 d.s.c. thermograms implies that the HX1000 phase in the blend is amorphous. It is generally believed that when a blend is partially miscible, two phases (one rich in component A and the second rich in component B) are observed. For such a system, both the T_gs are shifted inward from the values corresponding to the pure components. It should be noted that in the present study, only one T_g (that of the Ultem-rich phase) is observed to shift with composition.

In an effort to provide more support of partial miscibility the morphologies of Ultem/HX4000 and Ultem/HX1000 blend systems were studied and compared with those of the immiscible Ultem/Vectra blend system. The SEM micrographs of their fractured surfaces are shown in *Figures 5–7*. For the immiscible Ultem/Vectra composites, numerous microfibrils are observed to be pulled out from the surface (*Figures 5a* and *6b*). Large matrix voids generated by the pullout of microfibrils reveal the poor matrix/fibril interfacial adhesion for this system. In the case of the Ultem/HX4000 (*Figures 5c* and *6c*) and the Ultem/HX1000 (*Figure 5b* and *7*) *in situ* composites, no pulled out microfibrils are observed. Furthermore, the matrix shows a distinct tendency to form fibrils itself (*Figures 5–7*). It is most likely that due to the partial miscibility of the Ultem/HX4000 and the Ultem/HX1000 systems in these blends, an Ultem–LCP solid solution phase coexists with the LCP phase. Also, the interfacial adhesion appears to be good, which is suggestive of an interaction between LCP and the matrix. For this reason, no matrix voids and pulled-out fibrils are observed.

It has been reported in the literature that Ultem is miscible with PBI when solvent cast or co-precipitated, but phase separation takes place as the blend is heated to a temperature above or close to the T_g[19]. To understand the possible influence of annealing on the phase separation of the Ultem/HX4000 and the Ultem/HX1000 blends, injection moulded plaques were annealed at a temperature higher than the T_g of the Ultem and the LCPs (i.e. annealed at 250°C for 24 h) and then their glass transition behaviour before and after annealing was compared. As seen from *Figures 8* and *9*, in both blend systems no increase in T_g of the Ultem-rich phase is observed. For the Ultem/HX1000 70/30 blend (*Figure 9*),

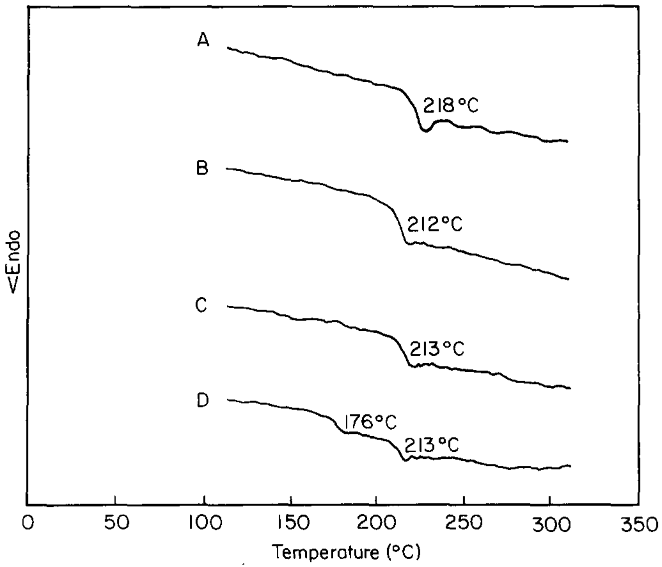

Figure 4 D.s.c. thermograms of Ultem/HX1000 blends with various composition ratios: A, 100/0; B, 70/30; C, 50/50; D, 30/70

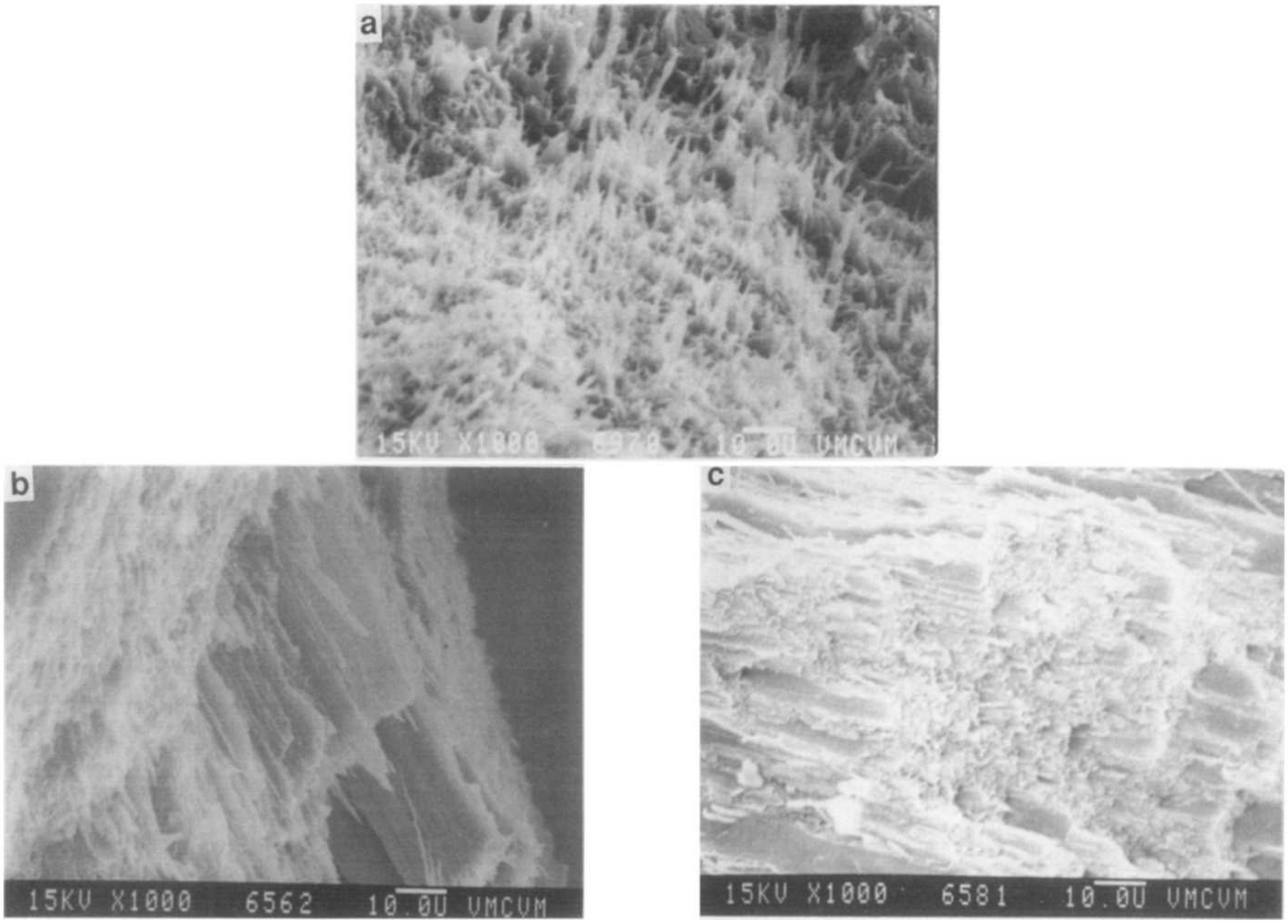

Figure 5 SEM micrographs of the fractured surfaces of injection moulded Ultem/LCP blend plaques: (a) Ultem/Vectra 70/30; (b) Ultem/HX1000 70/30; (c) Ultem/HX4000 70/30

the Ultem-rich phase remains at 223°C before and after annealing. For the Ultem/HX4000 70/30 blend (*Figure 8*), the T_g of the Ultem-rich phase decreases from 223°C (before annealing) to 215°C (after annealing). The above facts imply that no phase separation occurs for these two blend systems during heat treatment. The extent of the partial miscibility between the non-crystalline LCP HX1000 and Ultem remains almost unchanged. In the case of the Ultem/HX4000 70/30 blend, it appears that a part of the free HX4000 further 'dissolves' into the Ultem phase leading to a decrease in the T_g of the Ultem-rich phase.

We next consider whether there is any effect of mixing history on the shift in tan δ as well as on the morphology of the *in situ* composites. For this purpose the Ultem/HX4000 pellets extruded both from a single screw extruder (SSE) with a various number of passes and a twin screw extruder (TSE) were injection moulded. As seen from *Figure 10a* for the Ultem/HX4000 70/30 blend subjected to a single pass (SSE, 1 pass) a transition shoulder is observed at 180°C which matches the T_g of neat HX4000, indicating the presence of free HX4000 phase in the composite. For the materials with more than one pass through a mixing device (either through a SSE or a TSE, see *Figure 10b–d*) the T_g at 180°C has almost vanished. This implies that the extent of mixing between the Ultem and the HX4000 can be improved by increasing the number of passes. D.s.c. studies also lead to a similar conclusion (*Figure 11*). In the case of the Ultem/HX4000 70/30 blend when an SSE is used to prepare the blend pellets, the variation of the loss tangent (tan δ) with temperature for the second and third pass compositions (i.e. Ultem/HX4000 70/30 SSE, 2 passes and SSE, 3 passes) is almost the same. It is also virtually identical to that of Ultem/HX4000 70/30 TSE, 2 passes. This suggests that the maximum extent of miscibility between Ultem and HX4000 (when present in the ratio of 70/30) can be attained by two passes through an SSE. Further mixing by increasing the number of passes through an SSE or TSE does not lead to any further changes in the loss tangent (tan δ).

Irrespective of the composition of the composites, the diameter of the LCP microfibrils decreases upon increasing the number of passes (*Figures 12–14*). This morphological feature implies that the extent of dispersion of the LCP phase, and thus the fineness of the reinforcing fibrils in the *in situ* composites, can be improved by a suitable mixing process. It should also be noted that even though a single T_g is apparent, there are still two phases. Hence, mixing on a molecular scale has not occurred.

CONCLUSIONS

Partial miscibility between a PEI and an amorphous as well as a semicrystalline LCP was determined by measuring the shift in the T_g as determined by d.m.t.a. and d.s.c. With increasing concentration of the LCP in the PEI/LCP blends, the T_g of the PEI phase shifted to a lower temperature. A similar shift in the T_g was also

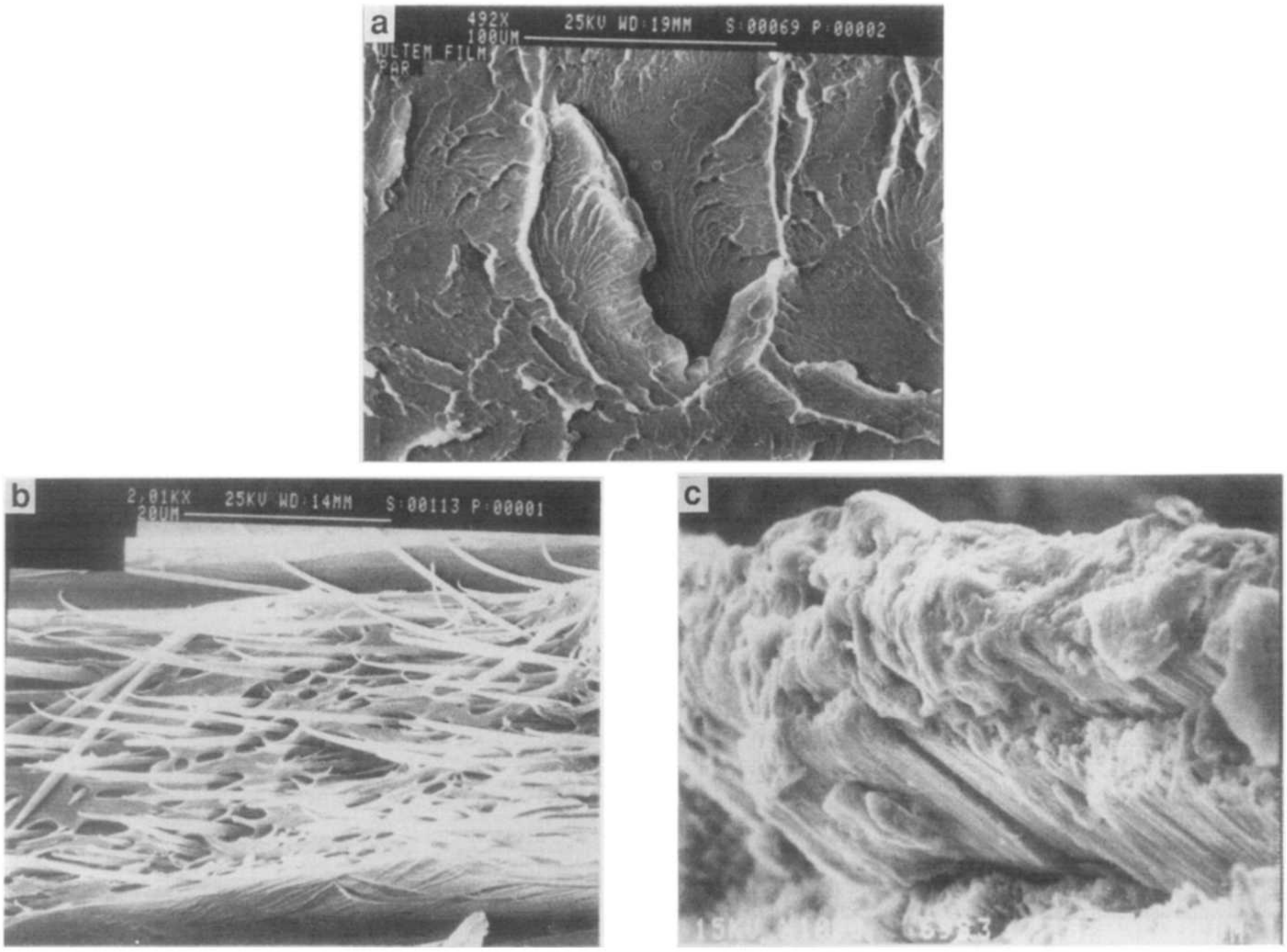

Figure 6 SEM micrographs of the fractured surfaces of extruded sheets: (a) Ultem; (b) Ultem/Vectra 90/10; (c) Ultem/HX4000 70/30

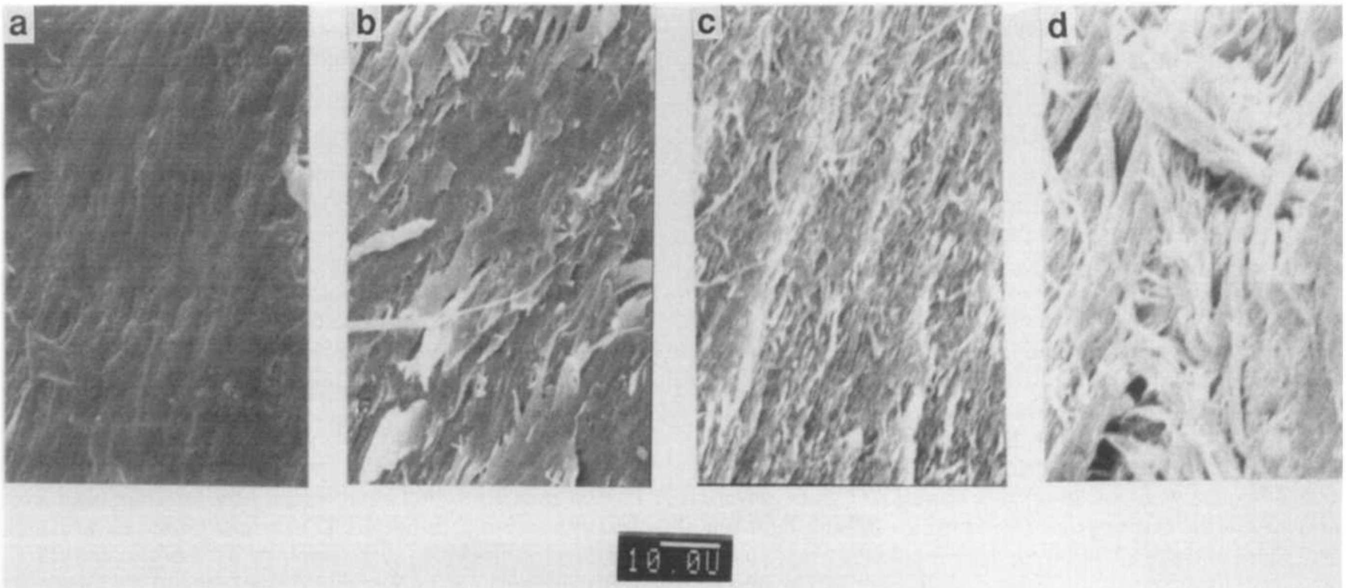

Figure 7 SEM micrographs of the fractured surfaces of injection moulded Ultem/HX1000 plaques: (a) Ultem/HX1000 70/30; (b) Ultem/HX1000 50/50; (c) Ultem/HX1000 30/70; (d) HX1000

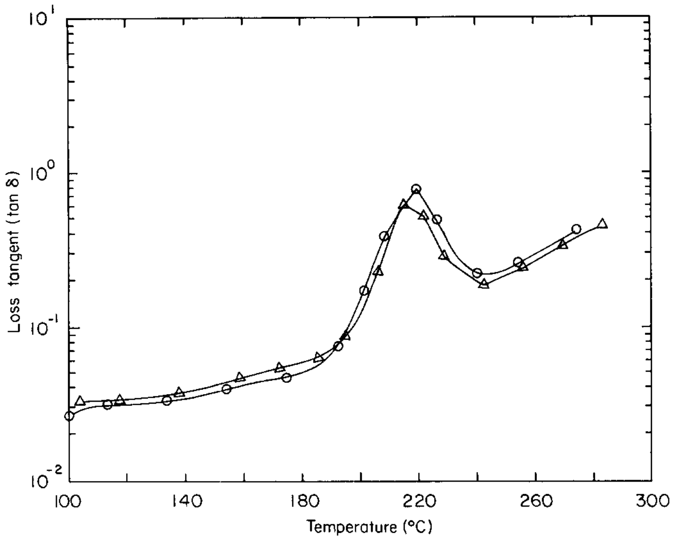

Figure 8 Loss tangent (tan δ) *versus* temperature for Ultem/HX4000 70/30 blend: ○, as injection moulded; △, annealed at 250°C for 24 h

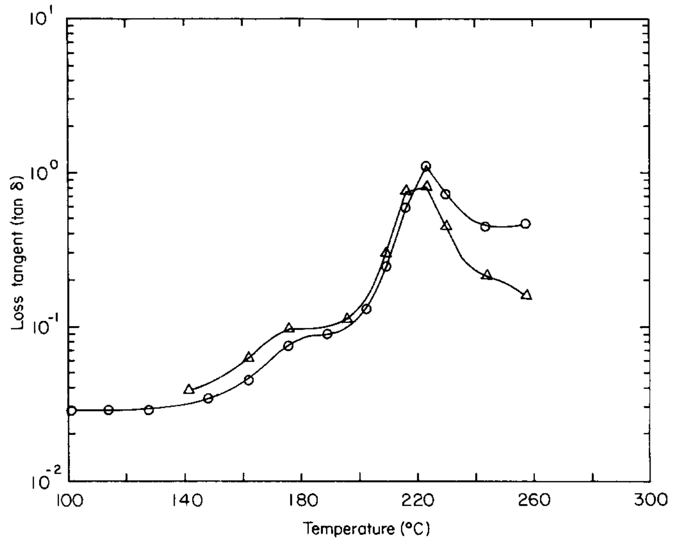

Figure 9 Loss tangent (tan δ) *versus* temperature for Ultem/HX1000 70/30 blend: ○, as injection moulded; △, annealed at 250°C for 24 h

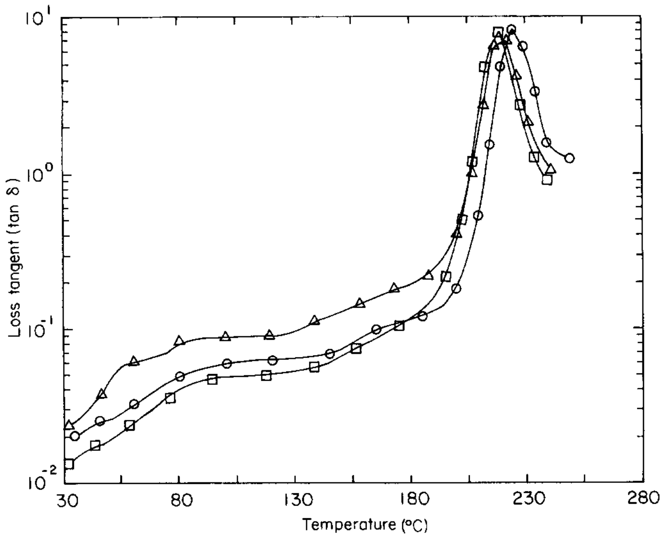

Figure 10 Mixing history effect for Ultem/HX4000 70/30 blend: ○, SSE, 1 pass; □, SSE, 2 passes and SSE, 3 passes (same curve for both); △, TSE, 2 passes

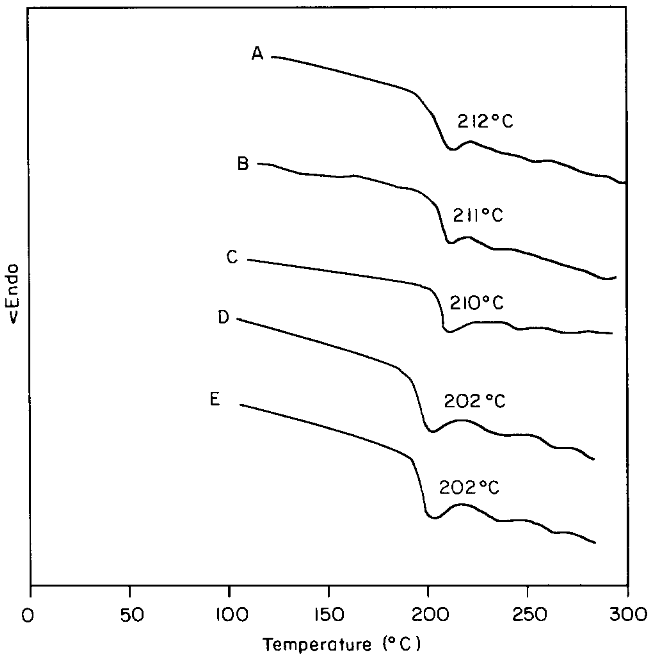

Figure 11 D.s.c. thermograms of Ultem/HX4000 blends with different mixing histories: A, 80/20 (SSE, 1 pass); B, 80/20 (SSE, 2 passes); C, 70/30 (SSE, 1 pass); D, 70/30 (SSE, 2 passes); E, 70/30 (TSE, 2 passes)

determined by means of d.s.c. It was found that the extent of mixing between the PEI and the LCP can be improved (to a certain extent) by increasing the number of passes through a single screw or passing the material through a twin screw extruder. Irrespective of the composition of the composites, the diameter of the LCP microfibrils decreased upon increasing the number of passes through the extruder. This morphological feature implies that the extent of the dispersion of the LCP phase, and thus the fineness of the reinforcing fibrils in the *in situ* composites, can be improved by a suitable mixing process. Morphologies of the partially miscible systems were found to be quite different from that of an immiscible system (which showed pull-out of LCP microfibrils and large voids where the microfibrils were pulled out of the matrix, revealing poor matrix/fibril interfacial adhesion). In contrast, partially miscible blends do not show the pulled out microfibrils and furthermore the matrix itself shows a distinct tendency to form fibrils. It can be concluded that due to partial miscibility in these blends, a PEI–LCP solid solution coexists with the neat LCP phase.

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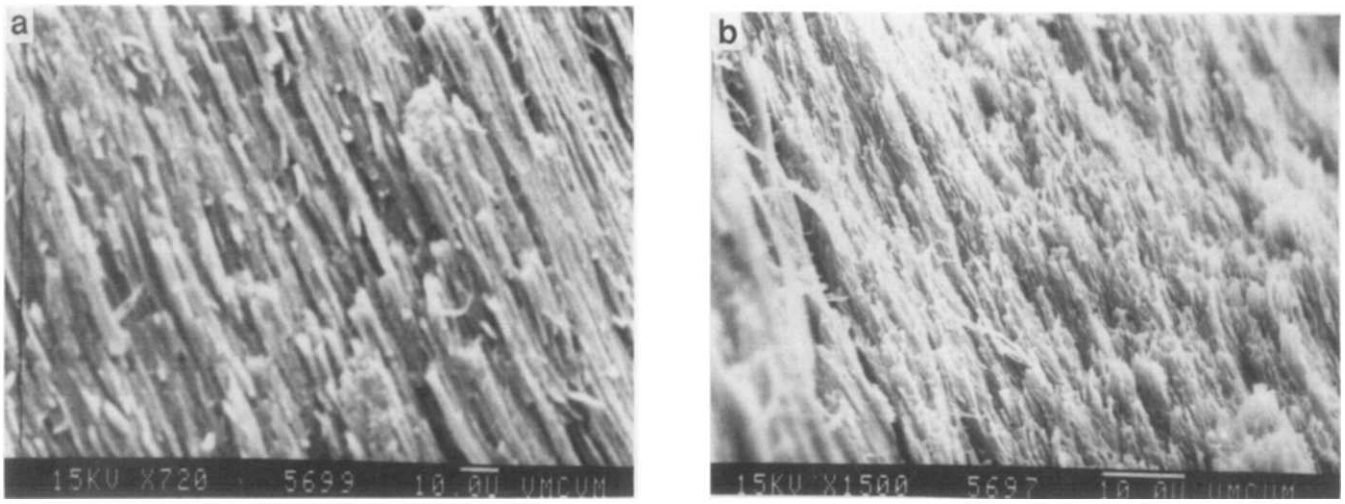

Figure 12 SEM micrographs of the fractured surfaces of injection moulded Ultem/HX4000 70/30 plaques: (a) TSE, 1 pass; (b) TSE, 2 passes

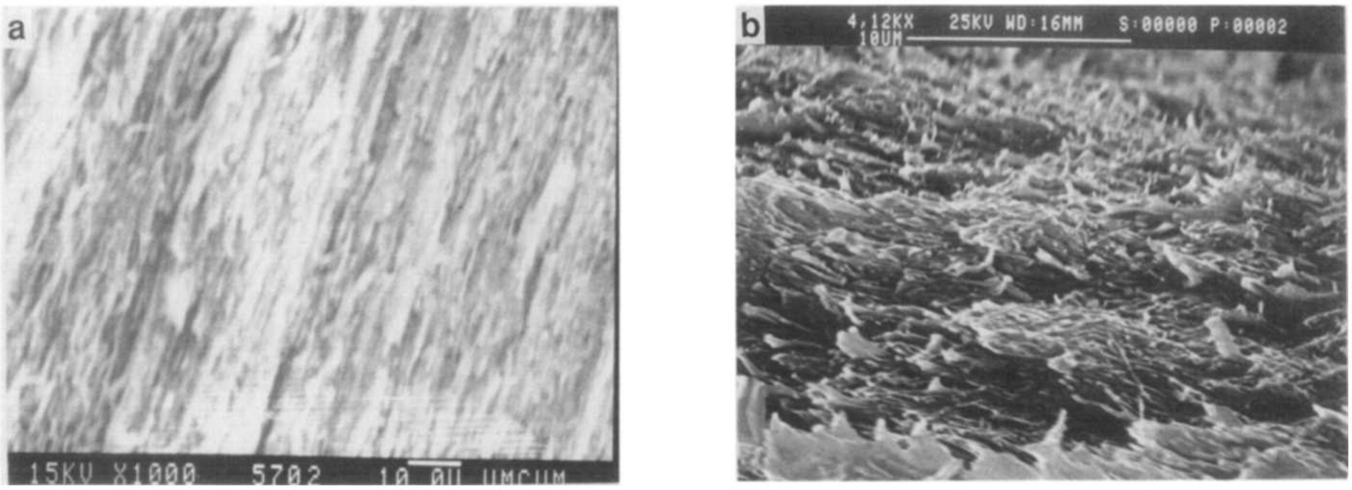

Figure 13 SEM micrographs of the fractured surfaces of injection moulded Ultem/HX4000 50/50 plaques: (a) TSE, 1 pass; (b) TSE, 2 passes

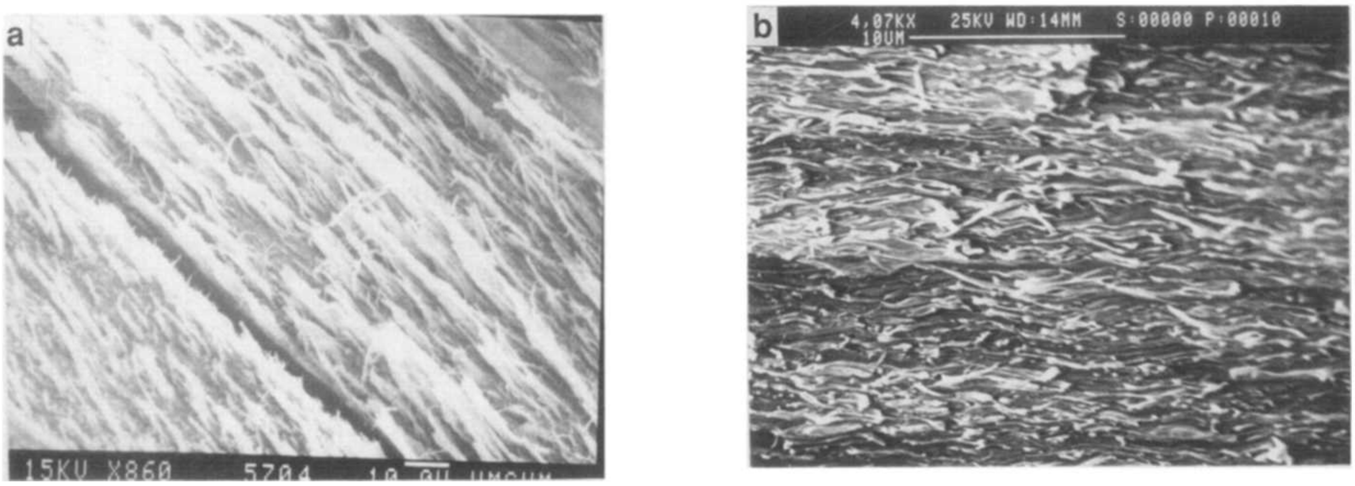

Figure 14 SEM micrographs of the fractured surfaces of injection moulded Ultem/HX1000 30/70 plaques: (a) TSE, 1 pass; (b) TSE, 2 passes

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