Miscibility and mechanical properties of poly(ether imide)/poly(ether ether ketone)/liquid crystalline polymer ternary blends

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This paper is concerned with a novel ternary blend composed of poly(ether imide) (PEI), poly(ether ether ketone) (PEEK) and a liquid crystalline polymer (LCP; HX4000, Du Pont). Different compositions were prepared by extrusion and injection moulding. Dynamic mechanical thermal analysis and the observation of the fracture surfaces, before and after annealing, allowed determination of the cold crystallization temperatures and miscibility behaviour of these systems. PEEK/PEI blends are known from previous studies to be miscible at all compositions. In this case it was observed that the PEEK/HX4000 blend was miscible up to 50 wt% HX4000 but partially miscible above this value. The PEI/HX4000 blends were found to be partially miscible in the whole concentration range. As a result, some ternary blend compositions exhibited only one phase, while others exhibited two phases. The measurement of the tensile properties showed that ternary blends with high modulus can be obtained at high LCP loadings, while compositions with high ultimate tensile strength can be obtained with high loadings of PEI or PEEK.

(Keywords: ternary blends; liquid crystalline polymers; miscibility; crystallization; morphology)

INTRODUCTION

Binary blends of flexible chain polymers and liquid crystalline polymers (LCP) have been studied intensively due to the potential to generate *in situ* reinforced composites. Polycarbonate (PC)[1,2], poly(ethylene terephthalate) (PET)[3] and high temperature and solvent resistant polymers like poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI)[5,6] have been blended mainly with liquid crystalline copolyesters based on PET and *p*-hydroxybenzoic acid and copolyesters of hydroxybenzoic and 2-hydroxy-6-naphthoic acid (Vectra A). These studies have been concerned with the correlation between processing conditions, fibril formation and enhancement of mechanical properties. Recently, blends of PEI with several different LCPs have shown a synergistic effect in that at intermediate compositions the modulus and strength of the blend are higher than the values for the LCP[7–9]. In the case of PEI/Vectra A the maximum in properties occurs at a composition of 90% Vectra A and 10% PEI. The two polymers appear to be immiscible based on dynamic mechanical thermal analysis (d.m.t.a.) and scanning electron micrographs. However, the blends based on PEI and polyesters based on terephthalic acid (TA), phenylhydroquinone (PHQ), hydroquinone (HQ) or PHQ, HQ and phenylethylhydroquinone (PEHQ), not only exhibit a positive deviation from the rule of mixtures for the modulus but show a maximum in tensile strength and modulus at a composition of about 70 wt% LCP and 30 wt% PEI[8]. Furthermore, it is indicated by d.s.c. results and d.m.t.a. data that these LCP/PEI systems are partially miscible[8]. Hence the possibility exists of forming compositions in which the rod-like reinforcement is more finely dispersed. There may also be some advantages in systems in which partial miscibility exists.

Ternary blends also present an attractive approach to the development of reinforced systems. Usually the main goal is to compatibilize two immiscible or partially miscible polymers through the use of a third polymer in which both are miscible. This has proved successful in systems like PC/styrene acrylonitrile (SAN) copolymer/aliphatic polyesters in which the partially miscible blend PC/SAN forms a ternary miscible blend with aliphatic polyesters, and in PC/phenoxy/polycaprolactone systems in which it is possible at high loadings of polycaprolactone to compatibilize the immiscible PC/phenoxy binary blend[10,11]. The phase equilibrium behaviour of a more complex system, poly(vinyl chloride) (PVC)/SAN copolymer/poly(methyl methacrylate) (PMMA) has also been studied[12]. In this case the PVC/SAN system is immiscible, the PMMA/SAN system is miscible, and the PVC/PMMA system is miscible at low PMMA contents, resulting in a ternary blend with a very narrow miscibility region. The phase behaviour of ternary blends has also been predicted

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theoretically[13–15] using the Flory–Huggins theory and composition independent interaction parameters, X_{ij}. However, we are not aware at this time of any studies of ternary systems in which one of the components is a LCP.

While PEI is apparently partially miscible with the LCPs based on the structures described above, it is known to be completely miscible with PEEK and polybenzimidiazole (PBI)[16,17]. The purpose of the work reported here is to explore the possibility of using PEI to make HX4000 miscible with PEEK. The results reported will address the dynamic mechanical and tensile properties of the ternary blends. A second paper will address more directly the phase behaviour, crystallization kinetics and the detailed morphology of these ternary blends.

EXPERIMENTAL

Materials

The polymers used in this study were a PEI (Ultem 1000) from General Electric, a PEEK (Victrex 450G) from ICI Co. and a LCP (HX4000, DuPont).

Blending

Before blending, the three polymers were vacuum dried at 120°C for 3 days. The binary blends, PEEK/HX4000 and PEI/HX4000, were prepared by injection moulding. The PEI/PEEK data were obtained from our earlier work[18]. In order to obtain ternary PEI/PEEK/HX4000 blends as homogeneous as possible, each composition was first tumbled in a container on a weight ratio basis, then melt blended, pelletized and finally injection moulded. Melt blending was performed in a Killion extruder (model KL-100). The screw had a ratio of length/diameter of 24, a diameter of 25.4 mm and a compression ratio of 3:1. The die diameter was 1.59 mm and the length was 25.4 mm. The following barrel temperatures were used: zone 1, 265°C; zone 2, 345°C; zone 3, 345°C; die section 1, 345°C; die section 2, 240°C. After extrusion the strands were pelletized and the pellets were again vacuum dried at 128°C for 6 days. Injection moulding was performed in an Arburg injection moulding machine (model 221-55-250) where rectangular plaques (75 mm × 80 mm × 1.78 mm) were obtained. At levels of LCP less than 60 wt%, the following barrel temperatures were used: zone 1, 365°C; zone 2, 350°C; zone 3, 365°C; zone 4, 370°C. The mould was held at 114°C. At levels of LCP above 60 wt% the barrel temperatures were: zone 1, 380°C; zone 2, 390°C; zone 3, 375°C; zone 4, 390°C. The mould was held at 119°C.

Annealing conditions

Measurements were carried out on two types of sample. In one case measurements were made on samples obtained directly from injection moulding. In these samples full crystallization may not have occurred in the semicrystalline components as a result of the cooling conditions in the mould. In the second case the injection moulded samples were annealed at the cold crystallization temperature, T_c, determined from dynamic data on the samples described above, for 3 days. The length of annealing time was chosen based on our experience with LCPs in which long annealing times were required to complete the crystallization process. In the case where no cold crystallization was observed, samples were annealed at 200°C for 5 days.

Dynamic mechanical thermal analysis

Rectangular strips (63.5 mm × 11.7 mm × 1.78 mm) were cut from the plaques and analysed in the torsional mode of a Rheometrics mechanical spectrometer (model RMS-800) at a frequency of 10 Hz and a strain of 0.05%. The temperature was varied between 40 and 300°C, at a heating rate of 3.5°C min^{-1}. Each composition was tested two or three times to determine the repeatability of the results.

Mechanical properties

Rectangular strips (80 mm × 15 mm × 1.78 mm) were also cut from the plaques along the flow direction and tested in an Instron tensile machine (model 4202). The strain was recorded using an extensiometer from MTS Systems Co. (model 63211B-20). Measurements were carried out at a crosshead speed of 0.20 cm min^{-1} following the procedures described in ASTM test number D-3039-76.

Scanning electron microscopy

Micrographs of the fracture surfaces of the blends were obtained with a Stereoscan 200 (Cambridge Instruments Ltd) scanning electron microscope. The samples were fractured under tension in liquid nitrogen and sputter coated with gold. The fracture surfaces were perpendicular to the injection moulding flow direction; the micrographs were taken at the central region of the samples.

RESULTS AND DISCUSSION

In order to analyse the miscibility behaviour of the ternary PEI/PEEK/HX4000 blends, a study was made first of the component polymers and of the binary systems. The mechanical properties of the binary blends have been published elsewhere[8,9] and will not be presented here.

Miscibility behaviour

The glass transition temperature, T_g, was evaluated at the point where tan δ had a maximum and the cold crystallization temperature, T_c, at the point where the storage modulus, G', had a sharp increase when measured as a function of temperature. The secondary relaxations, T_β and T_α, were taken as the peaks in tan δ that appeared before and after T_g, respectively.

Figure 1 shows the dynamic mechanical response of PEEK, PEI and HX4000. In *Figure 1a* it can be seen that the magnitude of the tan δ peak in the amorphous PEI is much higher than those of semicrystalline PEEK and HX4000, as expected. However, the HX4000 tan δ peak is broader and of smaller magnitude than that of PEEK. The β transitions of HX4000 and PEI are also broad. The β transition is not observed in our data for PEEK, because it occurs at −60°C (ref. 19). The PEI β transition has been attributed to oscillations propagated along the chain involving the aromatic and benzimide rings[16]. The origin of the β transition in HX4000 is unknown. The α peaks are related to the polymer's rotation inside the crystalline phase or with pre-fusion of the polymer[19]. These transitions are observed in PEEK

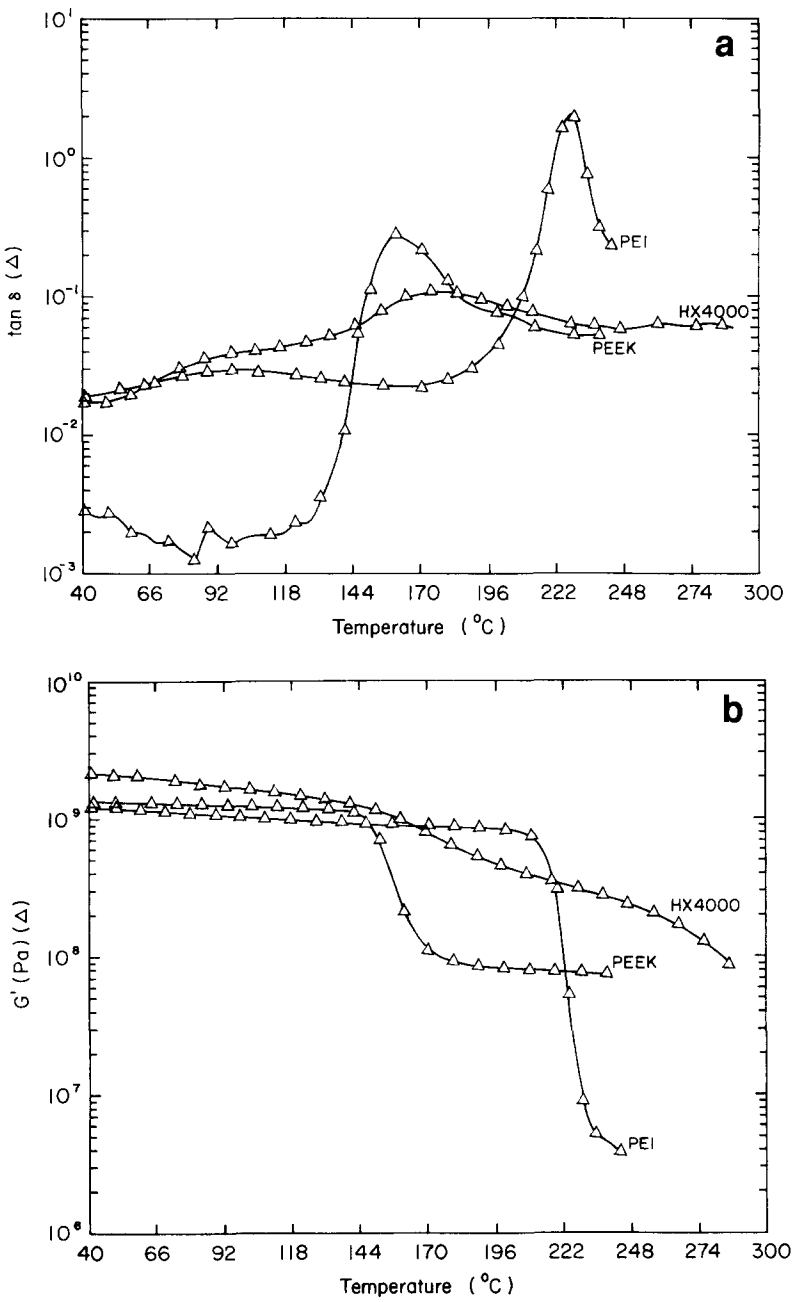

Figure 1 Dynamic mechanical behaviour of PEEK, HX4000 and PEI as determined in torsion using the RMS-800: (a) tan δ *versus* temperature; (b) storage modulus G' *versus* temperature

and HX4000. From *Figure 1b* it can be seen that the usual increase in the storage modulus, G', associated with cold crystallization, is not observed for PEEK. This may be due to the temperature at which cold crystallization occurs, which is near the glass transition temperature and disguises the phenomenon. Further changes in HX4000 were also not detected by this technique. *Table 1* shows these transitions as measured in the RMS-800.

D.m.t.a. results are presented for various binary blends including PEI/HX4000 and PEEK/HX4000. *Figure 2* shows the glass transition behaviour of unannealed blends of PEI/HX4000. Two T_gs were observed over the whole composition range. The high T_g is due to the PEI-rich phase while the low one is due to the HX4000-rich phase. Usually, in a blend, when the original T_gs of each polymer shift toward that of each polymer, partial miscibility is suggested and each coexisting phase is a mixture. In our case, we observe that the T_g of the PEI-rich phase decreases with the increase of the HX4000 concentration and approaches the T_g of the HX4000 phase. This is an indication that the HX4000 is acting as a plasticizer for the PEI and that the PEI phase is actually a mixture of both components. However, the T_g of the HX4000-rich phase remains almost unaltered, indicating that this phase is

Table 1 T_g, T_c and secondary relaxation temperatures (T_β and T_α) of the polymers (°C) as measured in torsion using the RMS-800

	T_g	T_c	T_β	T_α
PEEK	160	–	–	189
HX4000	176	–	87	244
PEI	229	–	98	–

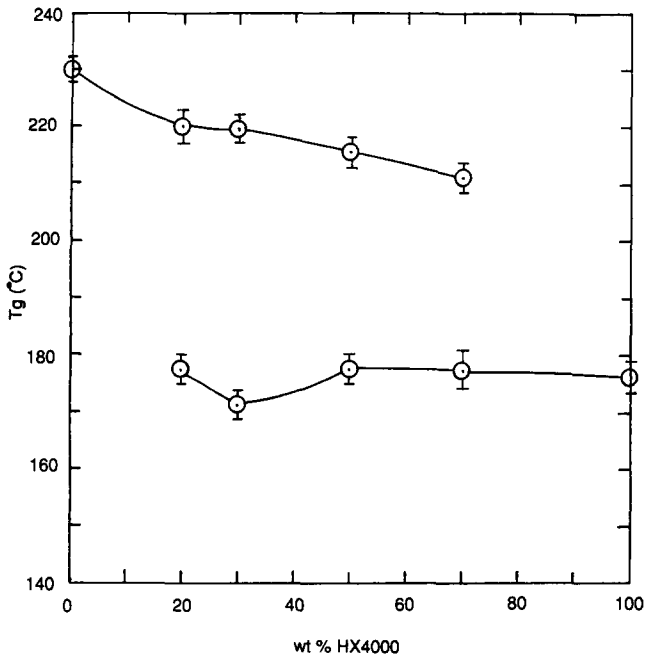

Figure 2 Glass transition temperatures of unannealed PEI/HX4000 blends as determined in torsion using the RMS-800

almost entirely LCP. We can picture this blend as an *in situ* composite in which the 'matrix' is made of PEI and HX4000, and the 'reinforcement' is made of the HX4000 fibrils.

Figure 3 shows the dynamic mechanical behaviour of unannealed blends of PEEK/HX4000. Resolution of the T_gs is poor due essentially to three factors: (i) the T_gs of the pure components are less than 20°C apart from each other; (ii) the HX4000 tan δ peak is small and broad; and (iii) cold crystallization occurs at temperatures intermediate to both T_gs. In *Figure 3a* it can be observed that for systems containing less than 50 wt% HX4000 only one glass transition exists, but for compositions greater than or equal to 50 wt% HX4000, two glass transitions appear. A relaxation peak at approximately 150°C is observed over the whole composition range. This relaxation peak can be attributed to the PEEK-rich phase that has been plasticized by the HX4000. As observed in *Figure 3b*, cold crystallization occurs in samples containing up to 50 wt% HX4000 as evidenced by the slight rise in G' after it reaches a minimum. The temperature at which cold crystallization occurs is not so readily evident in the figure, but is more apparent in the actual values measured. Specific values of the cold crystallization temperature are listed in *Table 2*. Induction of crystallization of one component of a blend by the other component has been observed in other binary blends[20]. When one of the components has a plasticizing effect on the other, as is the case for HX4000 on PEEK, it can induce crystallization by lowering the effective blend T_g and widening the $T_g - T_m$ interval. There is also the possibility that HX4000 can nucleate the crystallization of PEEK.

To corroborate the d.m.t.a. results, scanning electron micrographs of the fracture surfaces were obtained. *Figure 4a* is a micrograph of the fracture surface of a PEEK/HX4000 70/30 wt% blend. A single phase is observed confirming the d.m.t.a. result. The fracture surface of a PEEK/HX4000 30/70 wt% blend is shown in *Figure 4b*. Two fibrillar phases are observed: a HX4000-rich phase and a PEEK-rich phase. Based on these results, we can conclude that the PEEK/HX4000 blend, before annealing, is miscible up to 50 wt% HX4000, but partially miscible above this composition.

After annealing at 200°C a single T_g at about 170°C is observed over the whole composition range. In *Figure 4c* the fracture surface of an annealed PEEK/HX4000 70/30 wt% blend sample is shown. Again, a single phase is seen. The same texture is also observed in the fracture surface of the PEEK/HX4000 30/70 wt% blend (not shown). These results suggest that after annealing, this blend is miscible over the whole composition range. *Figure 5* shows the glass transition behaviour of these blends before and after annealing. These results are puzzling and are difficult to explain at present.

Next we turn our attention to the PEEK/PEI blends. As shown in *Figure 6*, a single glass transition temperature is observed over the whole composition range for annealed and unannealed samples. Similar results have been reported elsewhere[16,18]. After annealing, blends have an increase in T_g of 1–36°C due to the crystallization of PEEK. The addition of PEI to PEEK promotes cold crystallization up to 50 wt% PEI (see *Table 2*). In this case a dilution effect and consequently a decrease of the crystallization rates with an increase in PEI concentration are expected to be the cause.

The secondary relaxation temperatures are thought to be more sensitive to changes in the local environment of molecules and can show the intimacy of mixing between different polymer molecules[21]. In blends where specific interchain interactions may be relatively high, a shift in temperature and/or diminution of intensity of this secondary maximum can be observed[22,23]. In our case, this can be observed for the β transition of the PEEK/HX4000 and PEI/HX4000 blends with values summarized in *Table 2*. In the case of the PEEK/HX4000 blends, the β transition of the HX4000 is shifted towards lower temperatures. The origin of this transition in this particular LCP is unknown but usually is due to hindered segment rotation around the backbone bonds. Thus, the PEEK molecules are interacting in some way with the rigid HX4000 molecules, maybe through dipole–dipole bonding, allowing them to rotate at lower temperatures.

Table 2 T_c and secondary relaxation temperatures (°C) of the binary blends as measured in torsion using the RMS-800

Blend	T_c	T_β	T_α
PEEK/HX4000			
80/20	167	–	189
70/30	168	79	196
50/50	168	84	176
30/70	–	82	235
PEI/HX4000			
80/20	–	88	250
70/30	–	84	249
50/50	–	84	250
30/70	–	96	–
PEEK/PEI (18)			
90/10	182	–[a]	–[a]
70/30	206	–[a]	–[a]
50/50	229	–[a]	–[a]
30/70	–	–[a]	–[a]
10/90	–	–[a]	–[a]

[a]Data not available

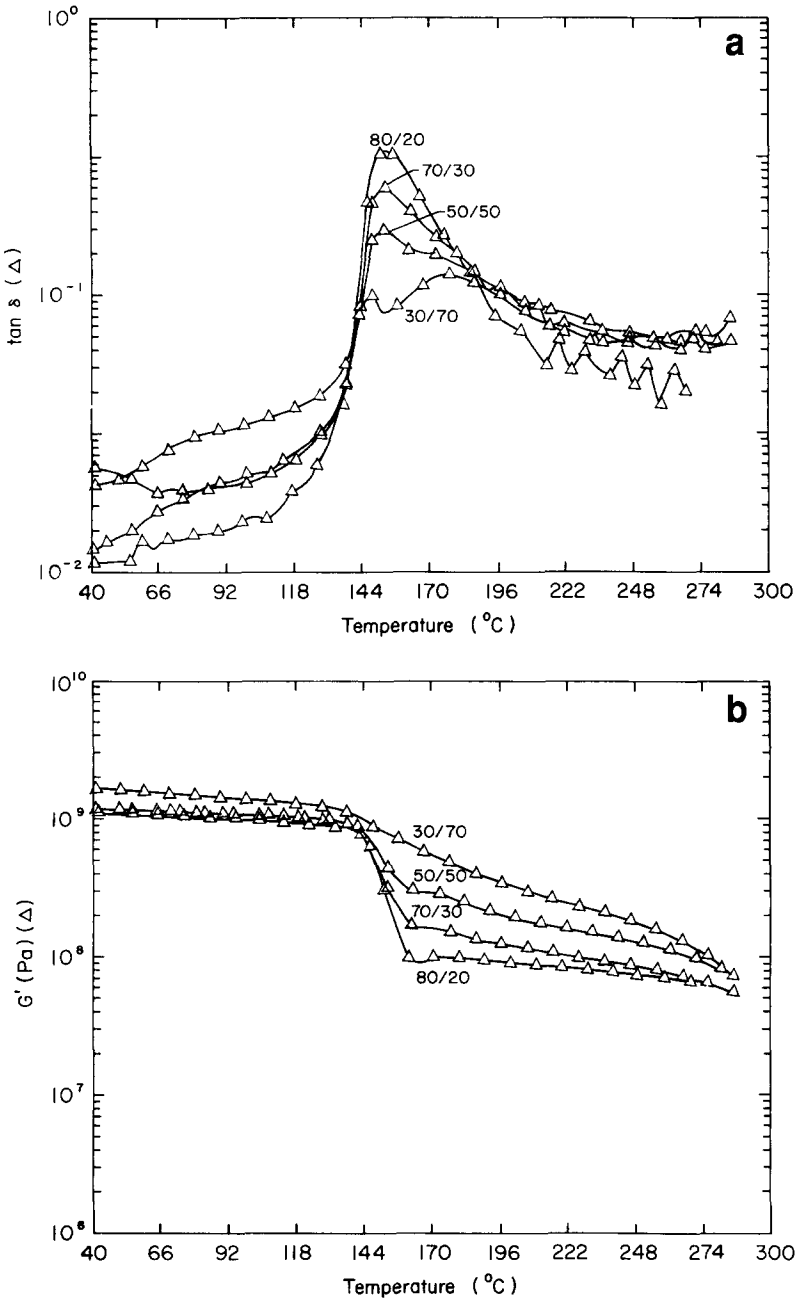

Figure 3 Dynamic mechanical behaviour of unannealed PEEK/HX4000 blends as determined in torsion using the RMS-800: (a) tan δ *versus* temperature; (b) storage modulus G' *versus* temperature

In the case of the PEI/HX4000 β transition, an erratic behaviour is observed. At 20 wt% HX4000, the β transition remains between the original values of HX4000 and PEI, but at 30 wt% and 50 wt% HX4000 it appears below these values, and at 70 wt% HX4000 it stays again between the original values but closer to the PEI value. No explanation can be given for this behaviour at present.

α Transitions are observed in all the binary blends containing PEEK and HX4000. In the case of the PEEK/HX4000 blends, this transition stays between the original values of the two polymers. In the case of the PEI/HX4000 blends the value is similar to that of the original HX4000 α transition, but somewhat higher. The shift in the secondary relaxation peaks seems to indicate an interaction in the systems involving PEEK/HX4000 or PEI/HX4000.

The dynamic mechanical behaviour of the ternary PEI/PEEK/HX4000 blends was also studied before and after annealing these blends. *Figure 7* shows the dynamic mechanical response of some of the ternary blends. The overlapping of the PEEK and HX4000 glass transition and the PEEK cold crystallization temperatures did not allow an accurate resolution of the peaks. *Figure 7a* shows that, before annealing, the main relaxation is actually composed of various overlapped peaks. After annealing, the presence of these overlapped peaks is not apparent (i.e. one can see only a single T_g). In *Figure 7b* it is observed that in compositions with high loadings of HX4000 or with high loadings of PEI which did not exhibit cold crystallization, the relaxation peaks can be resolved easily. In other compositions, such as that shown in *Figure 7c*, even when cold crystallization occurs, the peaks are resolved easily and accurately. Thus, the accurate resolution of the peaks is dependent on the blend composition. The analysis of the samples before annealing allows determination of the cold crystallization

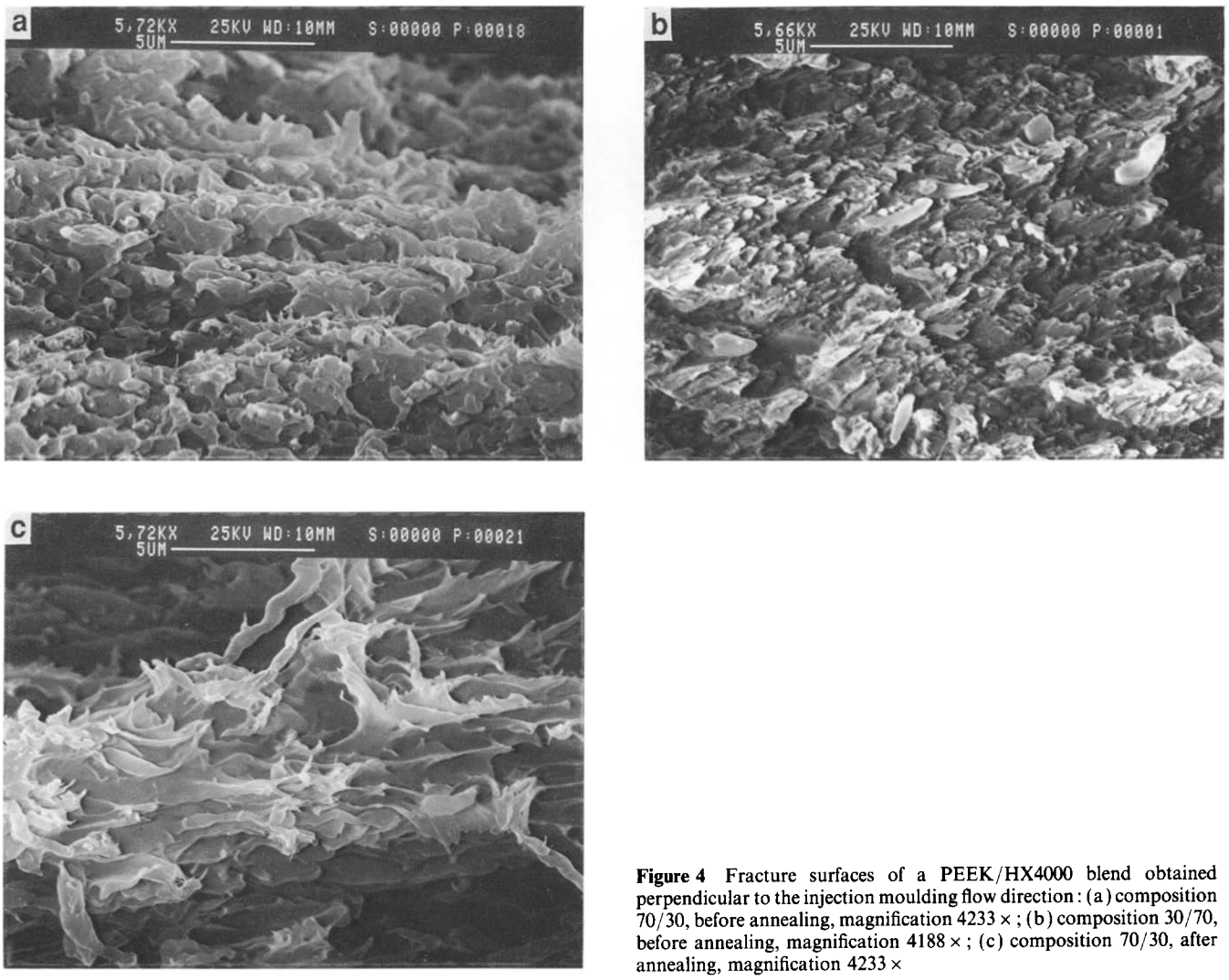

Figure 4 Fracture surfaces of a PEEK/HX4000 blend obtained perpendicular to the injection moulding flow direction: (a) composition 70/30, before annealing, magnification 4233 ×; (b) composition 30/70, before annealing, magnification 4188 ×; (c) composition 70/30, after annealing, magnification 4233 ×

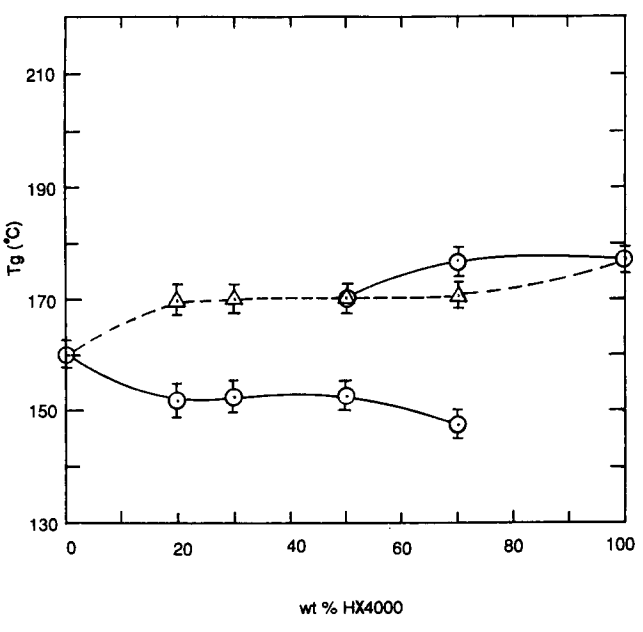

Figure 5 Glass transition temperatures of PEEK/HX4000 blends, before (○) and after (△) annealing, as determined in torsion using the RMS-800

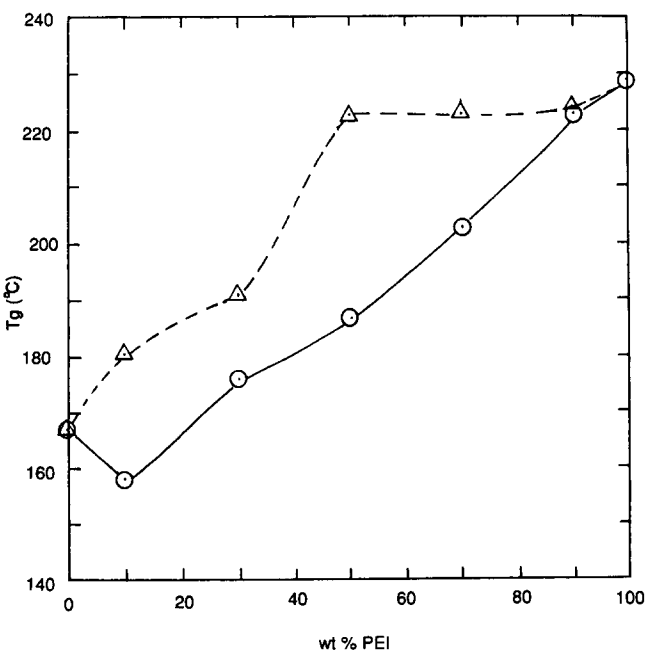

Figure 6 Glass transition temperatures of PEEK/PEI blends, before (○) and after (△) annealing, as determined in torsion using the RMS-800

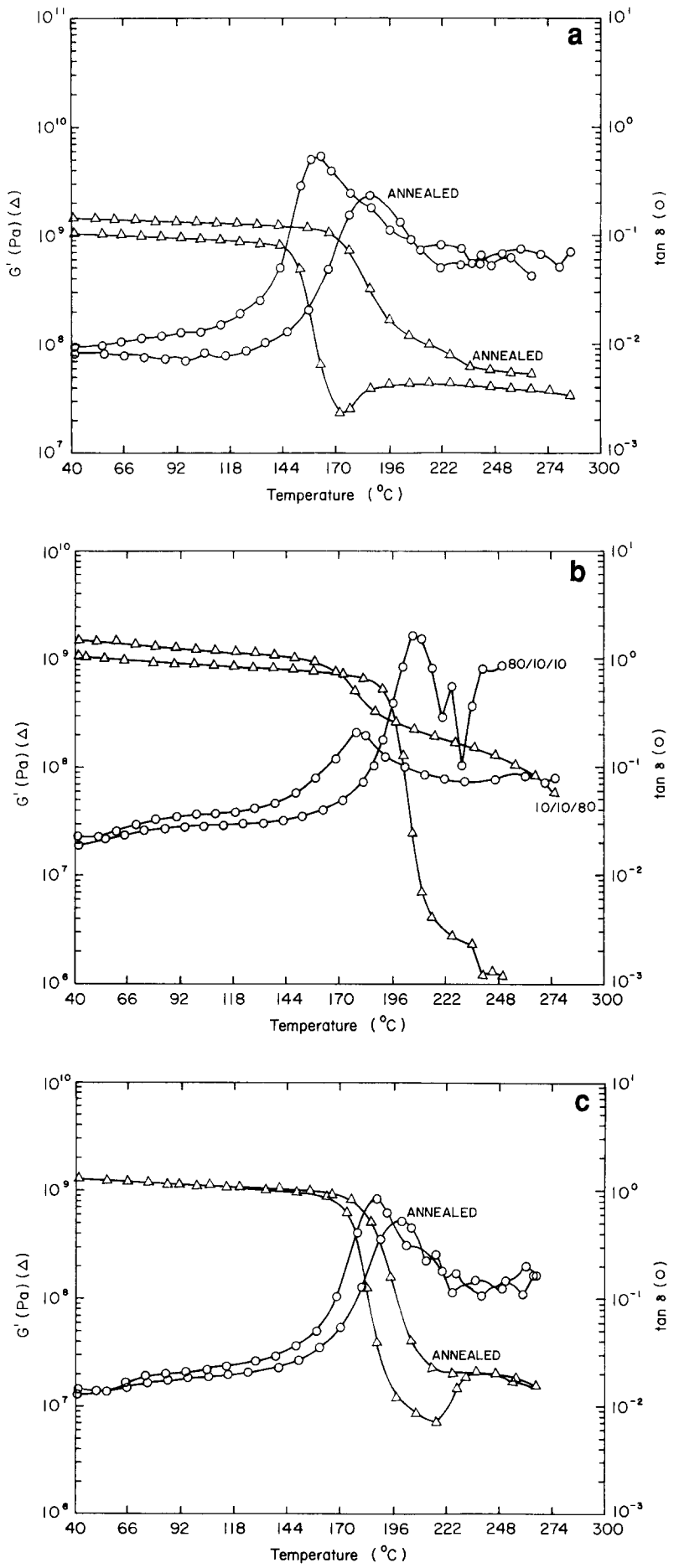

Figure 7 Dynamic mechanical behaviour of some of the ternary PEI/PEEK/HX4000 blends, before and after annealing, as determined in torsion using the RMS-800: (a) composition 10/80/10, before and after annealing; (b) compositions 10/10/80 and 80/10/10, before annealing; (c) composition 40/40/20, before and after annealing

Table 3 T_c and secondary relaxation temperatures (°C) of the ternary blends as measured in torsion using the RMS-800

Composition number	PEI/PEEK/HX4000 (wt%)	T_c	T_β	T_α
1	80/10/10	–	86	–
2	60/10/30	–	85	235
5	40/10/50	–	82	255
12	10/10/80	–	85	252
8	20/20/60	–	81	233
3	60/30/10	231	86	231
7	30/30/40	226	90	243
4	40/40/20	214	90	219
11	10/40/50	187	108	202
6	30/60/10	197	76	250
10	10/60/30	173	70	188
9	10/80/10	173	–	184

temperatures (T_c) for each composition. In *Table 3* these temperatures are presented together with the temperatures for the secondary relaxations. At low PEEK concentrations, no T_c is observed as would be expected due to a dilution effect. As the PEEK concentration increases, the cold crystallization temperature decreases. At the same PEEK concentration (compositions 3 and 7, 4 and 11, and 6 and 10 in *Table 3*), the blend with higher PEI and lower HX4000 contents shows the higher T_c due to the PEI dilution effect on the PEEK. This statement is based on the assumption that the observed G' increase is due only to the PEEK crystallization. However, it is also possible that annealing of the HX4000 occurs and cannot be detected by this method. The β transition stays between the original PEI and HX4000 transitions, indicating that interactions between PEI and HX4000 have occurred.

The dynamic mechanical tests were used to determine shifts, if any, in the T_g of the ternary blends before and after annealing and to deduce whether the compositions were miscible. The T_gs are plotted in the phase diagram given in *Figure 8* for unannealed samples and in *Figure 9* for annealed samples. For some compositions, it is observed that only a single T_g is present while for other compositions two T_gs are present. The presence of a single T_g is suggestive of miscibility between the components. Annealing seems to have a significant effect on miscibility as indicated by comparing the results in *Figures 8* and *9*.

For composition 3, a single T_g appears instead of the two distinct T_gs observed before annealing, indicating the formation of a single phase with a high T_g. Originally there were PEI- and HX4000-rich phases. After PEEK crystallization, it seems that miscibility of both phases also occurs and a high T_g, PEI-rich phase is formed. For composition 4, two T_gs are again observed, but with higher values of T_g than the originals. The HX4000-rich phase has an increase of 12°C and the PEI-rich phase an increase of 8°C. For composition 6, a single T_g is again observed, but with a higher value than that before annealing (a 29°C increase). For composition 7, a single T_g appears, instead of two distinct T_gs, at a temperature between the two original values. For composition 9, two T_gs are observed instead of the original single value, indicating that phase separation has occurred, perhaps due to crystallization. Two phases are now present, PEEK- and HX4000-rich phases, instead of the original PEEK-rich phase only. For composition 10, one T_g is observed, with an increase of 23°C over the value before annealing. For composition 11, one T_g is also observed with an increase of 19°C over the value before annealing. The one or two phases present after annealing have a T_g increase due to the PEEK crystallization.

Annealing has a significant effect on the magnitude of T_g. Before annealing the maximum T_g (209°C) is obtained with composition 2. Its value is 18% higher than the T_g of HX4000, 30% higher than the T_g of PEEK but 8.6% lower than the T_g of PEI. After annealing, composition 3 has the maximum T_g (217°C), being 22% higher than the T_g of HX4000, 35% higher than the T_g of PEEK but 5% lower than the T_g of PEI. Thus, a ternary composition of 60 wt% PEI, 30 wt% PEEK and 10 wt%

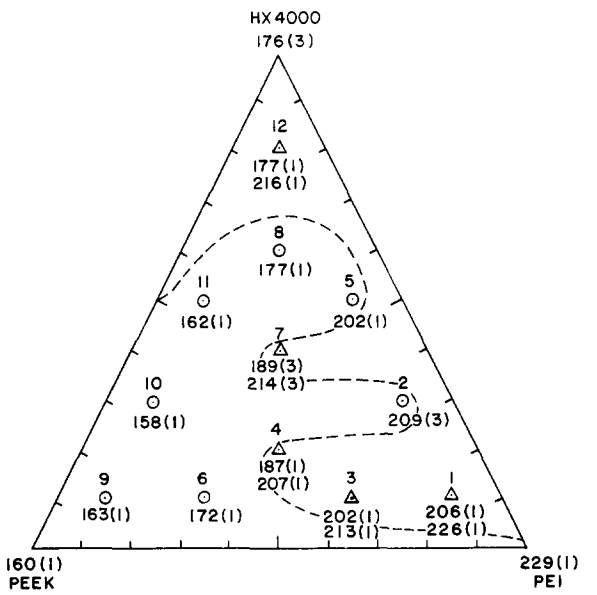

Figure 8 Glass transition temperatures (°C) of the ternary PEI/PEEK/HX4000 blends, before annealing, as determined in torsion using the RMS-800: ○, compositions with one T_g; △, compositions with two T_gs; – – –, approximate boundary between compositions with one and two T_gs. Standard deviations are given in parentheses

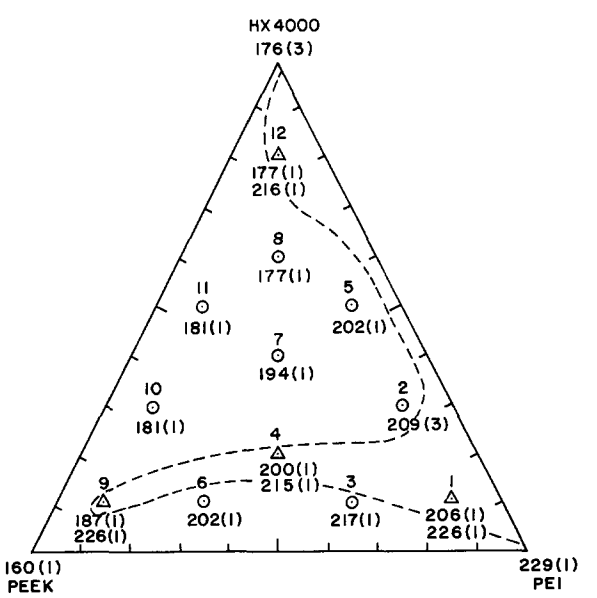

Figure 9 Glass transition temperatures (°C) of the ternary PEI/PEEK/HX4000 blends, after annealing, as determined in torsion using the RMS-800: ○, compositions with one T_g; △, compositions with two T_gs; – – –, approximate boundary between compositions with one and two T_gs. Standard deviations are given in parentheses

HX4000 is obtained after annealing, having a T_g higher than the T_gs of PEEK and HX4000 and almost the same as the T_g of PEI. Hence, materials with significant modifications of the T_g may be obtained for these systems by means of the composition ratio and annealing.

Tensile properties

The next question is whether one can obtain materials with unique physical properties by blending PEEK, PEI and HX4000. In particular, because of the apparent miscibility of certain compositions, it is desirable to know whether miscibility leads to materials with improved physical properties.

To facilitate the comparison of properties for different composition ratios, physical properties are plotted on ternary phase diagrams. *Figures 10* and *11* show the elastic moduli, E, ultimate tensile strength, UTS, and per cent elongation at maximum load, ε, of the ternary PEI/PEEK/HX4000 blends. Before annealing, the value of E (19.47 GPa) is obtained with composition 12. Its modulus is 29% higher than the HX4000 modulus, 369% higher than the PEEK modulus and 433% higher than the PEI modulus. Composition 4 presents the highest UTS (110.32 MPa), which is 11% higher than that of the HX4000, 33% higher than that of the PEEK and 13% higher than that of the PEI. The highest elongation (5.32%) is obtained with composition 6, being 638% higher than the HX4000 elongation, 20% higher than the PEEK elongation but 12% lower than the PEI elongation. Except for composition 4, the UTS of the blends decreases with increase of HX4000. No composition alone shows both a synergism in the tensile strength and elastic modulus, but those with the highest values are all partially miscible, with two observed T_gs.

After annealing the samples as described in the Experimental section, the highest elastic modulus (20.06 GPa) is again obtained with composition 12 (see *Figure 11*). Its modulus is 33% higher than the HX4000 modulus, 373% higher than the PEEK modulus and 449% higher than the PEI modulus. Composition 1 has the highest UTS (108.80 MPa), being 10% higher than that of the HX4000, 13% higher than that of the PEEK and 11% higher than that of the PEI. Composition 1 also has the highest elongation (4.33%), being 501% higher than that at HX4000, but still 15 and 28% lower than the PEEK and PEI elongations, respectively. Again, no composition alone shows a synergism in both elastic modulus and strength, but those with the highest values are all partially miscible with two observed T_gs. The annealing only increases the strength of compositions with 10 wt% HX4000, while for all others their strength is decreased.

The fracture surfaces taken perpendicular to the main flow direction of some of the ternary blends are shown in *Figure 12*. At high loadings of HX4000 (composition 12), before annealing, the fracture surface is fibrillar, with macrofibrils of diameter less than 1 μm (*Figure 12a*). After annealing (at 200°C for 3 days), the macrofibrils recoil (*Figure 12b*), probably due to the presence of PEI and PEEK in these macrofibrils. At low loadings of HX4000 and high loadings of PEEK (composition 9), before annealing, no macrofibril formation is observed, but instead the LCP-rich phase is seen to exist in a globular morphology (*Figure 12c*). Only one of these phases, the PEEK-rich phase, is detected by d.m.t.a.

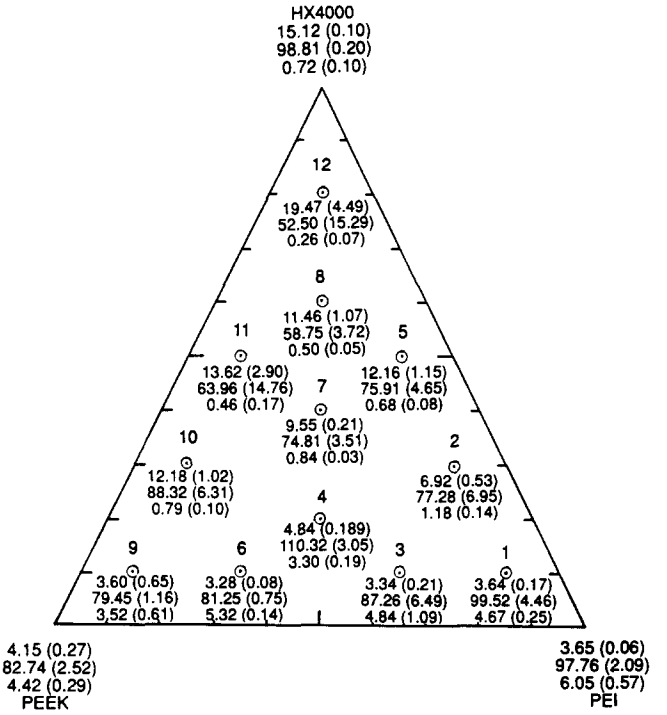

Figure 10 Elastic modulus (GPa), ultimate tensile strength (MPa) and elongation at maximum load (%) of the ternary PEI/PEEK/HX4000 blends, before annealing, for various composition ratios. The standard deviation of each value is given in parentheses

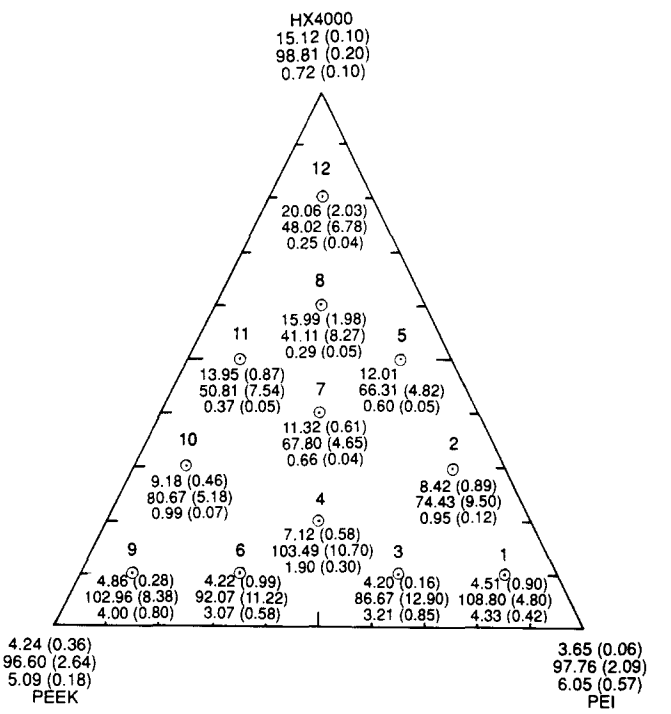

Figure 11 Elastic modulus (GPa), ultimate tensile strength (MPa) and elongation at maximum load (%) of the ternary PEI/PEEK/HX4000 blends, after annealing, for various composition ratios. The standard deviation of each value is given in parentheses

(composition 9, *Figure 8*). After annealing, the average size of the globular phase decreases (*Figure 12d*). This is probably due to the diffusion of the amorphous PEEK into the 'matrix' where it can crystallize. At high loadings of PEI (composition 1) no macrofibril formation is observed (*Figure 12e*). At a macroscopic level, phase separation is observed in the form of layers, as seen in

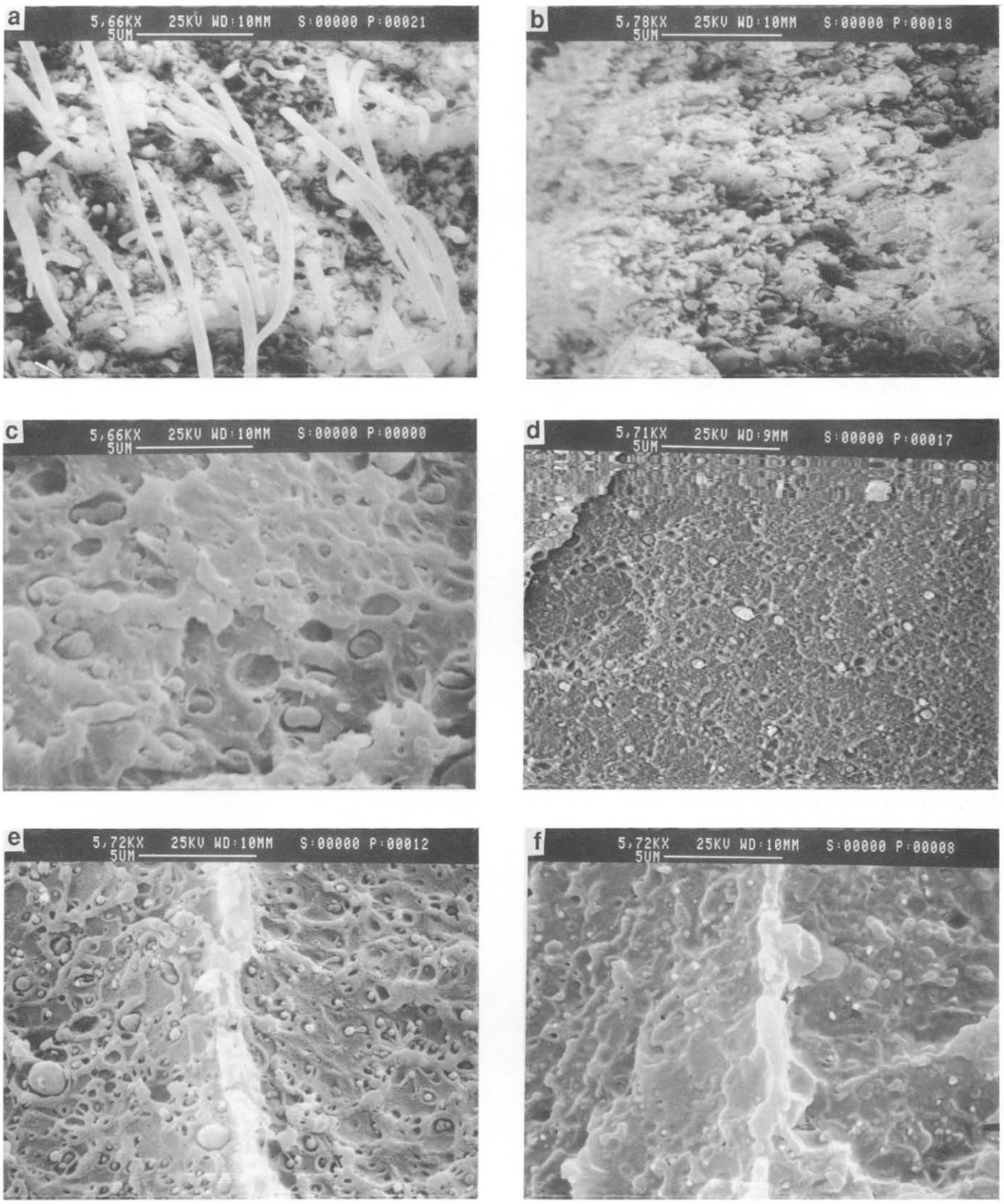

Figure 12 Continued on next page

the central strip of *Figure 12e*. After annealing, the average size of the globular phase again decreases (*Figure 12f*). This is also probably due to the diffusion of the PEEK phase into the PEI matrix so that it can crystallize. At intermediate compositions (composition 4) a more fibrous texture is observed (*Figure 12g*). Two phases are observed in agreement with the appearance of the two T_gs. It appears that the relation between morphology and mechanical properties is quite complex.

CONCLUSIONS

The results presented here must be considered with some reservations. The shifts in the different relaxation

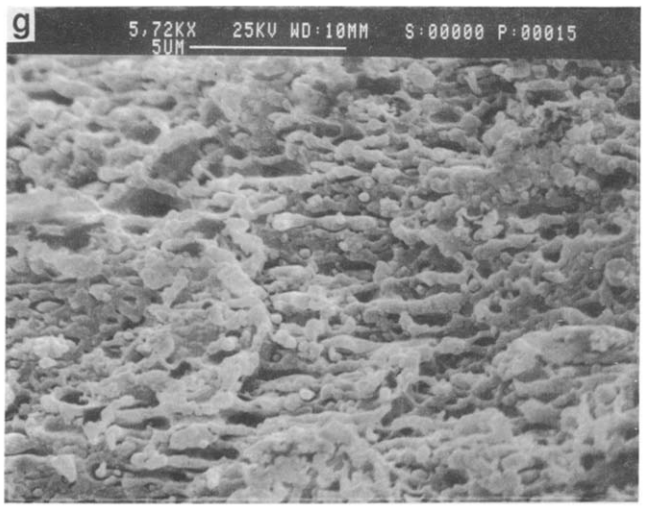

Figure 12 Fracture surfaces of ternary PEI/PEEK/HX4000 blends obtained perpendicular to the injection moulding flow direction: (a) composition 10/10/80, before annealing, magnification 4188×; (b) composition 10/10/80, after annealing, magnification 4277×; (c) composition 10/80/10, before annealing, magnification 4188×; (d) composition 10/80/10, after annealing, magnification 4225×; (e) composition 80/10/10, before annealing, magnification 4233×; (f) composition 80/10/10, after annealing, magnification 4233×; (g) composition 40/40/20, after annealing, magnification 4233×

temperatures were at times very small. Yet it is nearly impossible to detect these transitions using techniques such as d.s.c. In spite of these reservations, some preliminary conclusions can be made.

Before annealing, due to non-equilibrium conditions, the phase behaviour of the ternary blends was complex. This phase behaviour was the result of the miscibility of PEEK with PEI, the partial miscibility of PEI with HX4000 and the miscibility (up to 50 wt% HX4000) and partial miscibility (above 50 wt% HX4000) of PEEK with HX4000. Hence the observed miscibility behaviour is somewhat tentative and additional techniques such as *FT*i.r. should be used to establish interactions associated with miscibility.

After annealing, phase separation occurred due to PEEK crystallization. As a result of this the phase diagram of the ternary blends changed with a wide range of compositions showing a single T_g and hence miscibility. Overlapping of the T_gs of the binary components occurred. Composition 3 (60/30/10 PEI/PEEK/HX4000) had the highest T_g (217°C) whereas before annealing composition 2 (60/10/30 PEI/PEEK/HX4000) had the highest T_g (209°C).

The mixing of a rigid-rod LCP and a semicrystalline polymer is thermodynamically unfavourable due to the low combinatorial entropy change. However, the enthalpy of mixing can be negative or exothermic if certain specific interactions between polar groups are involved, and ΔG will then be negative in spite of the small entropy[21]. In our case, dipole–dipole intermolecular forces between the corresponding carbonyl groups may be responsible for these interactions[24]. The shift in the β transition temperatures can be interpreted as signifying the presence of these specific interactions.

The measurement of the tensile properties, after annealing, showed that it is possible to obtain ternary compositions that have an improvement in the elastic modulus and strength over the original values of the base polymers. High modulus compositions, like composition 12 (10/10/80 PEI/PEEK/HX4000) seem to be partially miscible and are composed of high loadings of LCP. A fibrillar fracture surface is observed in these compositions. The modulus of composition 12 is higher than the modulus of the component polymers. Compositions with high tensile strength like composition 1 (80/10/10 PEI/PEEK/HX4000) also seem to be partially miscible and are composed of high loadings of PEI or PEEK. No fibrillar fracture surface is seen in these compositions, but instead a globular morphology is observed. The strength of composition 1 was higher than that of the component polymers. Other partially miscible compositions (compositions 4 and 9) also had high ultimate tensile strengths. Composition 4 (40/40/20 PEI/PEEK/HX4000) had almost the same tensile strength as compositions 1 and 9, but a higher modulus. This composition exhibited a fibrillar structure as seen in the fracture surface.

In spite of any questions concerning miscibility, the fact that compositions can be obtained with a good balance of physical properties cannot be denied. Although miscibility and phase behaviour are scientifically intriguing for these systems, it is the physical properties which are of technical significance.

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