

# The effect of solvent uptake on the relaxation behaviour, morphology and mechanical properties of a poly(ether ether ketone)/poly(etherimide) blend

M. M. Browne, M. Forsyth and A. A. Goodwin\*

*Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia*  
 (Received 5 February 1996; revised 25 March 1996)

The effects of solvent uptake on the relaxation behaviour, morphology and mechanical properties of poly(ether ether ketone) (PEEK), poly(etherimide) (PEI) and a 50/50 PEEK/PEI blend have been investigated. Amorphous films were immersed in acetone at 25°C, 35°C and 45°C until equilibrium uptake was achieved. The films were then examined by wide angle X-ray scattering (WAXS), differential scanning calorimetry (d.s.c.), dynamic mechanical relaxation spectroscopy and mechanical testing. WAXS and d.s.c. revealed that the degree of solvent induced crystallinity in PEEK is constant with immersion temperature, whereas the degree of induced crystallinity in the 50/50 blend is strongly temperature dependent. The dynamic mechanical studies confirmed that a significant decrease in glass transition temperature results from the plasticizing effect of the solvent and that solvent and thermally crystallized samples have different relaxation characteristics. Mechanical property tests showed that the yield stress and tensile strength of the blend are dominated by PEEK and the degree of crystallinity, while the modulus is more sensitive to the extent of plasticization. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ether ether ketone); poly(etherimide); solvent uptake)

## INTRODUCTION

Replacement of metals by carbon fibre reinforced polymer matrix composites in automotive and aircraft applications has steadily been increasing<sup>1–3</sup>. The main benefits of plastic composites for these applications are weight reduction, lower costs and a reduced part count. Thermosetting polymer matrices are used extensively for such applications as they exhibit high solvent and temperature resistance. Thermoplastics are also candidates for such applications due to their inherent toughness. In high performance applications, materials must be able to withstand aggressive environments (e.g. oils, fuels, paint solvents). Therefore it is important to understand the effects of solvent exposure on the morphology and properties of high performance thermoplastics.

Poly(ether ether ketone) (PEEK) and polyetherimide (PEI) are both used in high performance applications. Semi-crystalline PEEK has excellent chemical resistance whereas PEI, which is an amorphous polymer, is soluble in a number of solvents. However PEI is by far the cheaper of these two polymers. It is well known that PEEK and PEI form a miscible blend at all compositions<sup>7</sup>. Therefore, by combining PEEK with PEI the potential exists for obtaining a novel, low cost, thermoplastic blend with enhanced chemical resistance. The effects of solvent uptake on the properties of PEEK have been extensively studied. Many solvents will diffuse into PEEK. The rate and amount of sorption has been

found to depend on several factors which include: solubility parameter, the hydrogen bonding index and other structural factors of the solvent, the amount of initial crystallinity of PEEK and the temperature at which sorption takes place.

Stober and Seferis<sup>4</sup> in particular found that PEEK will uptake solvent with a solubility parameter within a small range centred about 9.5 (cal cm<sup>-3</sup>)<sup>1/2</sup> and a hydrogen bonding index of about 3.1. Hay and Kemmish<sup>5</sup> studied the resistance of PEEK to environmental stress cracking. Environmental stress cracking was examined under constant stress by applying a drop of liquid directly on the surface of the undrawn region and the subsequent load drop was recorded as well as the number and size of the crazes formed. Liquids with solubility parameters of about 10 (cal cm<sup>-3</sup>)<sup>1/2</sup> were found to produce the maximum amount of load drop and cause crazing. Hay and Kemmish<sup>5</sup> also exposed unstressed PEEK specimens to a variety of organic liquids for extended periods. Solvents found to be absorbed to a large extent in amorphous PEEK were chloroform, bromoform, dichloroethane and tetrahydrofuran while carbon tetrachloride was not appreciably taken up by PEEK.

The initial crystallinity of PEEK is found to substantially reduce both the amount and the rate of solvent uptake. Amorphous PEEK has been found to absorb 20 wt% of toluene while 27% crystalline PEEK absorbed less than 0.2 wt% after immersion in toluene for 1500 h<sup>4–6</sup>. It is thus believed that the solvent is excluded from the crystalline regions and solvent diffusion only takes place in the amorphous regions. A number of

\* To whom correspondence should be addressed

studies have shown that PEI has poor resistance to aqueous bases and most automotive fluids<sup>2,3,7</sup>. One brief study on the environmental resistance of PEEK and PEI blends has been conducted by Harris and Robeson<sup>7</sup>. In this work test strips were placed under tension surrounded with cotton patches saturated in solvent and wrapped in aluminium foil to inhibit solvent evaporation. The time to rupture as a function of tensile stress was measured for various compositions of PEEK and PEI. The results obtained indicated a large improvement of the environmental resistance of a 70/30 wt% PEI/PEEK blend.

In this work we examine the effect of acetone sorption on the morphology and properties of PEEK, PEI and a 50/50 blend of PEEK and PEI. Previously<sup>8</sup> we have shown that blending reduces the initial diffusion coefficient of acetone into the 50/50 blend compared with the homopolymers.

## EXPERIMENTAL

### Materials

The PEEK used in this study was grade 381G, supplied by ICI Australia. The molecular weights are  $M_w = 73\,000$  and  $M_n = 30\,600$  (manufacturer's data). The PEI was Ultem 1000 supplied by GE Plastics with molecular weights of  $M_w = 30\,000$  and  $M_n = 12\,000$ <sup>9</sup>. A 50/50 blend, calculated as weight percent, was processed using a Haake Rheocord single screw extruder at 400°C. Pure PEEK and PEI were also extruded at 400°C and 300°C, respectively. The extruded materials were compression moulded at 400°C (300°C for PEI) and then quenched into ice/water to form amorphous sheets with thicknesses ranging from 0.2–0.6 mm. All samples were dried before blending, moulding and analysis. Thermally crystallized samples were produced by annealing at 250°C for 2 h.

### Dynamic mechanical analysis

The dynamic mechanical response of the samples was monitored using a Rheometric Scientific DMTA MKII in the bending mode, with dual cantilever geometry. Rectangular samples, measuring 30 mm × 10 mm × 0.5 mm, were scanned isochronally at a heating rate of 2°C min<sup>-1</sup> around the glass transition. The parameter tan δ was recorded between 0.03–200 Hz. Thermal scans were performed on samples immediately after exposure to solvent as well as after solvent desorption under vacuum.

### X-ray diffraction

Wide angle X-ray spectroscopy (WAXS) was performed on a Rigaku X-ray spectrometer using a Cu K<sub>α</sub> X-ray source and a Ni filter. The voltage was set at 40 kV and the current was set at 22.5 mA. A scan speed of 2° min<sup>-1</sup> with a sampling interval of 0.050° was used and the samples were scanned from 10–60°. Several isothermally crystallized PEEK and 50/50 wt% PEEK/PEI specimens were prepared and X-ray scattering curves obtained for comparison with the amorphous and acetone immersed samples. Samples immersed in acetone were allowed to desorb at room temperature overnight before use.

The mass fraction of crystallinity in the specimen was calculated using the method described by Young<sup>10</sup>. This method is based on the fact that the average electron

densities of polymers are closely proportional to the densities of the material<sup>15</sup>. This means that the ratio of the scattering intensities from the amorphous and crystalline phases of a material is approximately equal to the ratio of the masses of these phases. If, therefore, the area of the X-ray scattering curve due to scattering from the crystalline phase ( $A_c$ ) and from the amorphous phase ( $A_a$ ) can be separated, the mass fraction of crystallinity ( $x_c$ ) within the sample can be calculated from the equation

$$x_c = A_c / (A_a + A_c) \quad (1)$$

The applicability of this method to the determination of crystallinity in these blends will be discussed.

### Differential scanning calorimetry (d.s.c.)

Differential scanning calorimetry (d.s.c.) was performed on a Perkin-Elmer DSC7 using a scanning rate of 10.0°C min<sup>-1</sup> (between 100°C and 400°C). The d.s.c. was calibrated prior to use with high purity indium and zinc standards. Specimens of PEEK and 50/50 wt% PEEK/PEI that had been immersed at 25°C, 35°C and 45°C to equilibrium weight uptake as well as a PEI specimen that had been immersed at 45°C to equilibrium weight uptake were analysed. Approximately 10 mg of sample was used for analysis. As solvent was likely to desorb from the specimens during the analysis, open pans were used. To calculate the degree of crystallinity a value of 130 J g<sup>-1</sup> for the heat of fusion of 100% crystalline PEEK was used<sup>14</sup>.

### Mechanical properties

Mechanical testing was performed using an Instron tensile testing machine (model 4505) with a crosshead speed of 10 mm min<sup>-1</sup>. All specimens were tested at room temperature. Dumb-bell shaped tensile specimens were cut from sheets using a punch cutter with a gauge length of 25 mm and width of 3.8 mm. Amorphous, untreated specimens for each of PEEK, PEI, and the 50/50 blend were tested in addition to specimens that had been immersed in acetone at 25°C and 45°C until equilibrium weight uptake was achieved. Immersed samples were clamped in a fixed position while diffusion of acetone took place in order to prevent warping of the specimens. Five specimens for each sample were tested except in the case of PEI immersed in acetone, as many samples failed

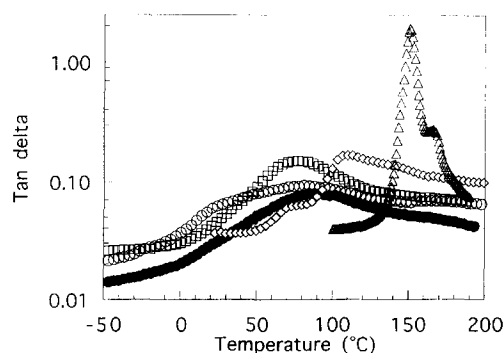


Figure 1 Dynamic mechanical spectra of amorphous PEEK ( $\Delta$ ); and PEEK immersed in various solvents at room temperature until equilibrium uptake; acetone ( $\diamond$ ); toluene ( $\square$ ); chloroform ( $\circ$ ); dichloromethane ( $\bullet$ ). All scans were carried out at 1 Hz and heating rate of 2°C min<sup>-1</sup>.

prior to testing. The gauge length and width were measured prior to testing using a digital micrometer accurate to  $10\ \mu\text{m}$ . Three different points were measured along the gauge length and the average taken. In order to prevent desorption during testing, immersed specimens were wrapped in cotton wool which had been soaked in acetone and then wrapped in aluminium foil. The yield stress was taken as the maximum stress that occurred before necking commenced and was calculated directly from the plots. Young's modulus and the % strain at break were calculated using the Instron 4500 Series software package. All results obtained were averaged and standard deviations obtained using a standard statistical approach.

## RESULTS AND DISCUSSION

### Glass transition behaviour

The relaxation characteristics of PEEK, after immersion to equilibrium at room temperature, were examined by dynamic mechanical analysis in the vicinity of the  $\alpha$ -relaxation. The temperature dependence of  $\tan\delta$  is shown in Figure 1 along with thermal scans of PEEK immersed in other solvents and amorphous, untreated PEEK. The solvent exposed samples were scanned immediately upon removal from liquid in order to minimize solvent desorption during scanning. The glass transition of the solvent exposed PEEK is shifted to lower temperatures, is considerably broadened and is lower in intensity; these features are consistent with plasticization of the matrix and solvent induced crystallization. Chloroform and dichloromethane both produce broader and lower maxima, compared with acetone and toluene. This may be associated with the greater uptake of these solvents by PEEK (>50% by weight) whereas acetone and toluene are absorbed to around 20% by weight. All solvents induce the same degree of crystallinity at 35°C which is reported to consist of tighter and more organized crystals than those resulting from thermal crystallization<sup>11</sup>. Since solvent desorption occurs during the thermal scan the  $T_g$ s shown in Figure 1 (taken as the temperature at the  $\tan\delta$  peak), which range from 100°C for acetone to 77°C for toluene, are not representative of each sample at equilibrium uptake.

Acetone exposed (at 45°C) PEEK, PEI and a 50/50 blend were also examined by dynamic mechanical analysis after drying under vacuum at 100°C for 14 days to remove as much solvent as possible. The spectra

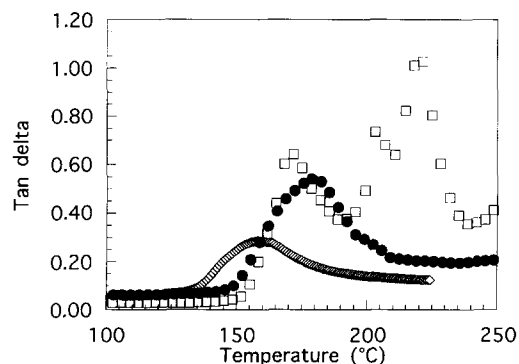


Figure 2 Dynamic mechanical spectra of PEI (□); PEEK (◇) and a 50/50 PEEK/PEI blend (●) after desorption of acetone

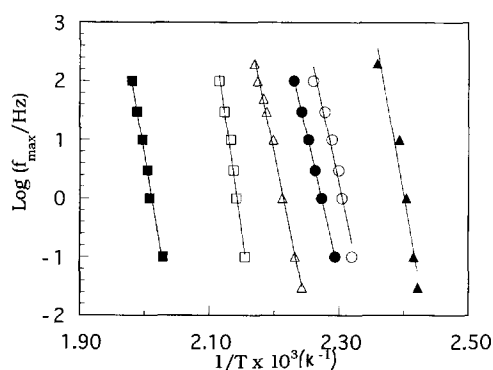


Figure 3 Arrhenius plot of amorphous, solvent crystallized and thermally crystallized samples: amorphous PEEK (▲); solvent crystallized PEEK (○); thermally crystallized PEEK (●); amorphous 50/50 PEEK/PEI blend (△); solvent crystallized 50/50 PEEK/PEI (□); thermally crystallized 50/50 PEEK/PEI blend (■); data are taken from dynamic mechanical studies at various frequencies; solid lines are fits to Arrhenius equation

are shown in Figure 2. Subsequent weighing studies showed that while PEEK fully desorbed acetone, PEI retained approximately 3.0 wt% of solvent and the 50/50 blend retained approximately 2.5 wt% of solvent. This indicates the high affinity of acetone for PEI. The PEI scan shows two maximums in  $\tan\delta$ , at 173°C and 220°C. The first is associated with the glass transition of PEI containing a residual amount of acetone while the second maximum is close to that of amorphous, untreated PEI. This indicates that complete acetone removal from the PEI matrix occurs above  $\approx 170^\circ\text{C}$ .

The relaxation behaviour of solvent and thermally crystallized materials can be compared in the form of an Arrhenius plot with  $\log(\text{frequency})$ , based on dynamic mechanical studies at various impressed frequencies, being plotted against the corresponding reciprocal temperature, as shown in Figure 3. In this figure the data refers to solvent crystallized samples scanned after drying under vacuum to remove solvent. For PEEK and the 50/50 blend the relaxation temperatures of solvent and thermally crystallized samples are offset to higher temperatures, compared with the amorphous state. This is due to the local constraining influence of the crystallites on the amorphous chains<sup>12</sup>. The thermally crystallized samples are offset to higher temperatures, compared with the solvent crystallized material (the greater offset in the solvent exposed 50/50 blend may be due to residual solvent causing a slight plasticization). In a similar study on PEEK, Kalika *et al.*<sup>13</sup> reported the greatest offset for solvent crystallized PEEK, in contrast to our findings. However, their results were obtained from exposure to acetone vapour at 25°C, whereas our findings come from complete immersion in acetone at 45°C. As the data shown in Figure 3 are linear over the temperature range of measurement, an activation energy,  $E_{\text{act}}$ , for the  $\alpha$ -relaxation was obtained by fitting to the Arrhenius equation. For amorphous PEEK, as well as PEEK crystallized thermally and by solvent,  $E_{\text{act}}$  was found to be  $\approx 1000\ \text{kJ mol}^{-1}$ . For the 50/50 blend in the amorphous, thermally crystallized and solvent crystallized states,  $E_{\text{act}}$  was found to be  $1018 \pm 28\ \text{kJ mol}^{-1}$ ,  $1213 \pm 57\ \text{kJ mol}^{-1}$  and  $1456 \pm 78\ \text{kJ mol}^{-1}$ , respectively. The differences in relaxation temperature and  $E_{\text{act}}$  indicates that the morphologies of solvent and thermally crystallized samples are of a significantly different character.

Determination of crystallinity

WAXS was performed on PEEK and the 50/50 wt% blend that had been immersed at all temperatures as well as PEI that had been immersed at 35°C and 45°C. No crystallization of PEI was found to occur at these temperatures. WAXS measurements of thermally crystallized PEEK and blend specimens were also performed for comparison. WAXS spectra for the untreated and 45°C immersed PEEK and blend are shown in Figures 4 and 5. A blend spectrum with the appropriate amorphous halo subtracted is shown in Figure 6. This spectrum shows broader features than the equivalent thermally crystallized blend which is also shown in this figure. Similar broadening of the crystallization peaks in pure PEEK has been previously observed<sup>11</sup>. The apparent amorphous halo in the crystallized samples is shifted, when compared with the measured amorphous spectrum prior to crystallization. Therefore direct subtraction of these curves as required by Young's method (see Figures 4 and 5) was not appropriate.

In order to obtain a more precise fit it was necessary to shift the amorphous curves. Other methods of determining crystallinity have used deconvolution of the peaks by fitting Gaussian curves to obtain approximate crystalline and amorphous areas<sup>10,15</sup>. It is thought that by using the original amorphous halo of untreated specimens instead of Gaussian curve distributions the errors may be

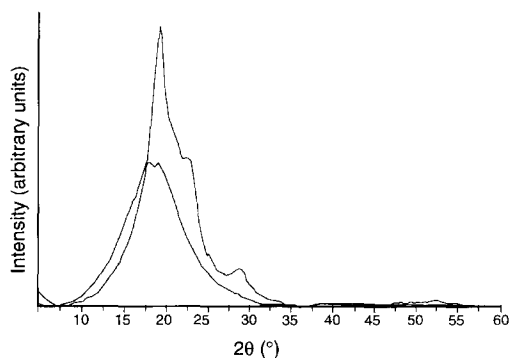


Figure 4 WAXS spectra for amorphous PEEK (lower curve) and PEEK immersed in acetone until equilibrium uptake at 45°C (upper curve)

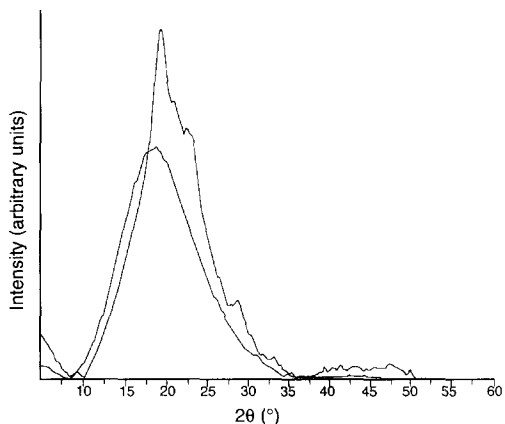


Figure 5 WAXS spectra for amorphous 50/50 PEEK/PEI blend (lower curve) and a 50/50 PEEK/PEI blend immersed in acetone until equilibrium uptake at 45°C (upper curve)

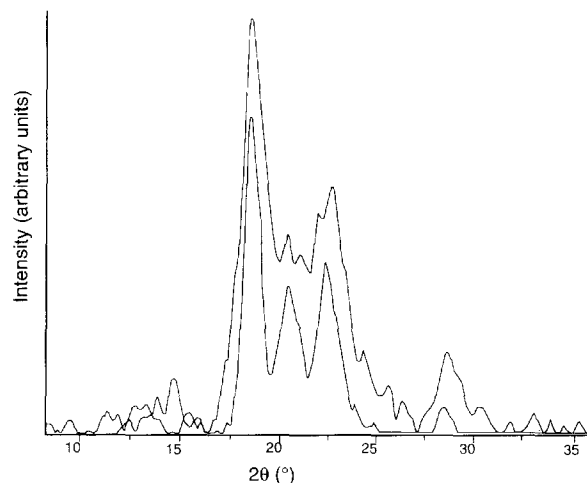


Figure 6 Corrected WAXS spectra for thermally crystallized 50/50 PEEK/PEI blend (lower curve) and solvent crystallized 50/50 PEEK/PEI blend (upper curve). The appropriate amorphous spectra have been subtracted from the 'as measured' spectra

reduced, especially in the case of the blend specimens, as the amorphous PEI X-ray scattering curves were found to be asymmetric. The differences in the amorphous curves for the PEEK and PEI specimens further complicate the analysis. As the PEEK component only of the blend crystallizes the amorphous fraction of the material will be PEI rich compared with that of the original specimen. As PEI was found to have a slightly asymmetric amorphous X-ray scattering curve a greater fraction of PEI in the amorphous phase could strongly affect the shape of the semicrystalline blend amorphous halo. Subtraction of various combinations of blend and PEI amorphous curves was performed in order to obtain an average estimate of the fraction of crystallinity and an estimation of the error involved. Similar effects were also observed in thermally crystallized samples.

One possible explanation for the changes in the amorphous halo may be that, although the amorphous phase of a material has no true long range order, local short range order exists (i.e. certain distances between neighbouring atoms are more probable than others). It is therefore likely that any changes in the amorphous morphology due to crystallization will affect the probability distribution and hence the amorphous halo. Previously it has been thought that crystallinity in PEEK due to thermal treatment and solvent induced crystallinity have differing morphologies<sup>16</sup>. The difference in the shape of the apparent amorphous halo of thermally crystallized specimens and the apparent amorphous halo of solvent induced crystalline specimens is consistent with this view and further supports the conclusion reached from the d.m.a. analysis.

The WAXS and d.s.c. results, summarized in Table 1, show that solvent induced crystallinity in PEEK does not increase significantly with temperature. The d.s.c. results suggest a higher degree of crystallinity than the WAXS results. This may be a result of further crystallization during the d.s.c. scan, although no exothermic peak was observed in this case. Values of crystallinity similar to that determined by WAXS have previously been reported in solvent crystallized PEEK immersed in acetone and other solvents to equilibrium uptake<sup>11,13,16</sup>. The blends at 25°C and 35°C did show evidence of

**Table 1** Degree of crystallinity obtained from WAXS and d.s.c.

| Immersion temperature (°C) | Specimen | Weight % crystallinity (of PEEK) |        |
|----------------------------|----------|----------------------------------|--------|
|                            |          | WAXS                             | D.s.c. |
| 25                         | PEEK     | 18 ± 4                           | 34 ± 3 |
| 35                         | PEEK     | 23 ± 7                           | 32 ± 2 |
| 45                         | PEEK     | 21 ± 7                           | 37 ± 2 |
| 25                         | Blend    | 2 ± 2                            | 14 ± 7 |
| 35                         | Blend    | 22 ± 6                           | 28 ± 6 |
| 45                         | Blend    | 36 ± 8                           | 42 ± 4 |

**Table 2** Temperature dependence of the diffusion coefficient and weight increase for PEEK, PEI and 50/50 blend (taken from ref. 8)

| Temperature (°C) | Sample      | Diffusion coefficient ( $10^{15} \text{ m}^{-2} \text{ s}$ ) | Weight increase (%) |
|------------------|-------------|--|---------------------|
| 25               | PEEK        | 3.4 ± 1.0  | 13.1 ± 0.2          |
|                  | 50/50 blend | 1.2 ± 0.2  | 20.2 ± 0.2          |
|                  | PEI         | 2.4 ± 0.6  | 17.6 ± 0.4          |
| 35               | PEEK        | 8.4 ± 3.4  | 14.2 ± 0.1          |
|                  | 50/50 blend | —  | 20.7 ± 0.4          |
|                  | PEI         | 5.2 ± 0.6  | 18.8 ± 0.4          |
| 45               | PEEK        | 100 ± 309  | 12.1 ± 0.2          |
|                  | 50/50 blend | 6.2 ± 1.5  | 16.9 ± 0.3          |
|                  | PEI         | 6.8 ± 0.5  | 19.4 ± 0.4          |

crystallizing during the d.s.c. scan (possibly resulting from plasticization by residual solvent in the blend). Crystallization in the d.s.c. may account for differences between the degree of crystallinity determined by the two methods.

WAXS and d.s.c. results indicate a large increase in crystallinity in the blend with increasing immersion temperature. There are several factors which may affect the amount of crystallinity obtained in the blend. In order that PEEK can crystallize in the blend, PEI must diffuse away from the PEEK crystallization front and PEEK must also diffuse to the crystallization front. The rate of crystallization of the blend will therefore depend on the mobility of the amorphous phase. The rate of diffusion is slowed also by the necessary expulsion of PEI from the growing crystalline region. As the amorphous phase contains PEI, a polymer with a higher  $T_g$  than PEEK, the rate of diffusion of PEEK and therefore the rate of crystallization in the blend will be slowed in comparison with that of pure PEEK. It has been reported by several investigators that the rate of thermal crystallization of PEEK within a blend specimen is

substantially reduced by the presence of PEI<sup>17-19</sup>. These effects may show a greater dependence on temperature.

#### *The effect of blending and temperature on solvent diffusion*

Previous results have shown a substantial reduction in the initial diffusion coefficient of the blend in comparison to its constituent homopolymers, PEEK and PEI. Table 2 presents the results and is taken from ref. 8. The initial diffusion coefficient can be considered representative of the rate of diffusion into the glassy, unplasticized thermoplastic materials. The rate of diffusion of solvent into glassy polymers is dependent on several factors; the mobility, the free volume and the affinity the polymer has to the solvent. The mobility of a polymer generally increases the closer the temperature is to the  $T_g$ .

PEI has a  $T_g$  considerably higher than that of PEEK and hence is found to have a slightly lower initial diffusion coefficient in comparison to PEEK. The 50/50 wt% blend also has a  $T_g$  substantially higher than that of PEEK and so it is not surprising that the initial diffusion coefficient for the blend is significantly lower than that of PEEK. However,  $T_g$  is not the only factor in determining the diffusion coefficient of the blend. A possible explanation for the decrease in the rate of initial solvent uptake in the blend in comparison to its constituent homopolymers is due to the increase in density on blending reported by Chen and Porter<sup>18</sup>. This negative deviation from linearity indicates favourable intermolecular interaction between PEEK and PEI and a decrease in available free volume for solvent to diffuse through.

As induced crystallinity has been found to increase with increasing temperature both for PEEK and the blend, the effect of increasing temperature is to decrease the wt% uptake at equilibrium in these samples. Although increasing crystallinity with increasing immersion temperature accounts for the reduction of weight uptake with temperature for the blend and for PEEK, it does not account for the decrease in weight uptake for PEI with increasing temperature as no crystallinity was observed in PEI. It was however observed for PEI, that dissolution of the polymer took place close to equilibrium weight uptake.

#### *Mechanical properties*

Tensile tests were carried out on amorphous untreated specimens of PEEK, PEI and 50/50 wt% PEEK/PEI as well as all specimens immersed to equilibrium in acetone at 25°C and 45°C. Table 3 shows the tensile strength, yield stress, Young's modulus and percent strain at break obtained in each case.

**Table 3** Mechanical properties of PEEK, PEI and 50 wt% PEEK/PEI blend

| Conditions       | Specimen | Tensile strength (MPa) | Yield stress (MPa) | Young's modulus ( $\times 10^2$ MPa) | % Strain at break |
|------------------|----------|------------------------|--------------------|--------------------------------------|-------------------|
| Untreated        | PEEK     | 56 ± 2                 | 41 ± 1             | 13.4 ± 0.5                           | 245 ± 15          |
|                  | PEI      | 91 ± 4                 | 50 ± 2             | 14.0 ± 0.9                           | 14 ± 1            |
|                  | Blend    | 70 ± 4                 | 45 ± 2             | 13.4 ± 0.07                          | 50 ± 50           |
| Immersed at 25°C | PEEK     | 33 ± 2                 | 27 ± 2             | 9.60 ± 0.5                           | 286 ± 35          |
|                  | PEI      | 1.5 ± 0.9              | 0.6 ± 0.6          | 0.83 ± 0.9                           | 4 ± 2             |
|                  | Blend    | 16 ± 0.9               | 15.0 ± 0.9         | 5.0 ± 0.3                            | 17 ± 6            |
| Immersed at 45°C | PEEK     | 38 ± 4                 | 32 ± 2             | 1.0 ± 0.2                            | 6.8 ± 0.5         |
|                  | PEI      | 5 ± 3                  | 5 ± 3              | 0.3 ± 0.2                            | 304 ± 12          |
|                  | Blend    | 28 ± 3                 | 24 ± 5             | 1.0 ± 0.2                            | 5 ± 1             |

The mechanical properties of the as moulded specimens indicate PEEK is a more ductile material at room temperature than PEI. The results of tensile strength and yield stress for the blend exhibit values almost exactly intermediate between those of its constituent homopolymers. This is consistent with previous work<sup>7</sup>. The percentage strain at break, however, is reduced considerably from the weighted mean. This is perhaps due to the reduction of specific volume and free volume that occurs upon blending.

Plasticization of a polymer by solvent is likely to affect the mechanical properties by reducing the elastic modulus and tensile strength and enhancing ductility. The effects on the specimens after total immersion at 25°C in acetone until equilibrium were consistent with plasticization except that, for the blend and PEI, percentage elongation (and thus the ductility) was substantially reduced. This can be attributed to the tendency of PEI to dissolve in the solvent. PEEK, on the other hand, has a higher percent strain at break after immersion at 25°C to equilibrium than as-moulded specimens. PEEK is also found to have a substantially higher tensile strength and yield stress in comparison to PEI even though these properties were initially higher for PEI. These differences can again be attributed to dissolution of PEI as well as to induced crystallization of PEEK.

Immersion in acetone at 45°C resulted in crystallization of the PEEK and blend samples, as discussed earlier, thus resulting in an increased yield stress and tensile strength. However, the modulus decreases significantly in all cases. This indicates that the modulus is influenced primarily by the extent of plasticization and not by the degree of crystallinity. This is particularly evident when comparing PEEK immersed at 25°C and 45°C. In all the solvent immersed cases, the fact that the mechanical properties of the blend (with the exception of the strain at break) are close to those of PEEK, whereas for PEI the mechanical properties are severely degraded, indicates that the PEEK component is dominating the mechanical behaviour of the blend.

The different strain-at-break behaviour of PEEK immersed at 45°C may be due to the presence of random flaws in some samples causing failure at low strains. PEEK has been reported as being susceptible to solvent stress cracking. The low strain at break exhibited by the blend may be attributed to the lower ductility of PEI resulting in similar behaviour in the blend.

## CONCLUSIONS

From previous work<sup>8</sup> we have shown that the rate of solvent uptake in a 50/50 PEI blend is reduced compared with the homopolymers although the equilibrium weight uptake of acetone is still greater than in pure PEEK. The decrease in the equilibrium weight uptake with increasing

temperature of immersion, in the case of PEEK and PEEK/PEI blend, can be correlated with the increased degree of solvent induced crystallization. WAXS and d.s.c. have shown that, in the blend, the degree of solvent induced crystallization is very temperature dependent whereas the degree of crystallinity in pure PEEK is constant with immersion temperature. This may be due to the decreased rate of crystallization in the blend.

This work has shown that care must be taken when determining the degree of crystallinity by WAXS, particularly with blends, since the amorphous halo appears to be sensitive to the composition and morphology of the amorphous region.

The d.m.a. experiments confirmed that a significant decrease in  $T_g$  occurs as a result of plasticization by the absorbed acetone. This will also account for the ability of the PEEK to crystallize when  $T_g$  drops below the immersion temperature. D.m.a. also showed that solvent and thermally crystallized samples have different relaxation characteristics, and that crystallization increases the  $T_g$  relative to the amorphous state.

Mechanical property measurements for the solvent immersed blend samples indicate that the Young's modulus, yield stress and tensile strength are dominated by the PEEK component. In addition, tensile strength and yield stress are strongly dependent on the degree of crystallinity whereas Young's modulus is more sensitive to the degree of plasticization. The strain at break in the blends is, however, dominated by the less ductile PEI.

## REFERENCES

- 1 Horn, W. J., Skaikh, F. M. and Soeganto, A. *AIAA J.* 1989, **27**, 1399
- 2 Baxter, D. F. *Adv. Mat. Pro.* 5/90, 37-47
- 3 Long, E. R. and Collins, W. D. *Polym. Eng. Sci.* 1988, **28**, 823
- 4 Stober, E. J. and Seferis, J. C. *Polym. Eng. Sci.* 1988, **28**, 634
- 5 Hay, J. N. and Kemmish, D. J. *Polymer* 1988, **29**, 613
- 6 Wolf, C. J., Bornmann, J. A. and Grayson, M. A. *J. Polym. Sci. (B)* 1992, **30**, 113
- 7 Harris, J. E. and Robeson, L. M. *J. Appl. Polym. Sci.* 1988, **35**, 1877
- 8 Browne, M. M., Forsyth, M. and Goodwin, A. A. *Polymer* 1995, **36**, 4359
- 9 Hudson, S. D., Davis, D. D. and Lovinger, A. J. *Macromolecules* 1995, **28**, 1759
- 10 Young, R. J. and Lovell, P. A. 'Introduction to Polymers', 2nd edition, Chapman and Hall, London, 1991
- 11 Wolf, C. J., Bornmann, J. A., Grayson, M. A. and Anderson, D. P. *J. Polym. Sci. (B)* 1992, **30**, 251
- 12 Jonas, A. and Legros, R. *Macromolecules* 1993, **26**, 813
- 13 Kalika, D. S., Nickell, R. K., Krishnaswamy, R. K. and Barton, B. E. *J. Polym. Sci. (B)* 1994, **32**, 759
- 14 Blundell, D. J. and Osborn, B. N. *Polymer* 1983, **24**, 953
- 15 Kakudo, M. and Kasai, N. 'X-ray Diffraction by Polymers', Elsevier, Tokyo, 1972
- 16 Michele, A. and Vittoria, V. *Polymer* 1993, **34**, 1898
- 17 Crevecoeur, G. and Groeninckx, G. *Macromolecules* 1991, **24**, 1190
- 18 Chen, H. L. and Porter, R. S. *Polym. Eng. Sci.* 1992, **32**, 1870
- 19 Hsiao, B. S. and Sauer, B. B. *J. Polym. Sci. (B)* 1993, **31**, 901