Characterization and exposure of polyether-etherketone (PEEK) to fluid environments

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The sorption and desorption behaviour in fluids is described for polyetheretherketone (PEEK) films of different crystallinity. Water, Skydrol, and methylene chloride were used as fluid environments at two temperatures, and the weight gain of the films as a function of time was recorded. Density, thermomechanical, and dynamic mechanical measurements were made for the films before and after the fluid exposure. The results confirmed the general solvent resistance of PEEK. However, exposure to methylene chloride produced two significant effects: plasticization and additional crystallization for incompletely crystallized films. Exposure to different fluids was shown to suppress the exhibited thermomechanical transitions of these films. For the incompletely and fully crystallized films a comparison was made for crystallinity values obtained by the differential scanning calorimetric and density gradient techniques. Finally, dynamic mechanical and sorption in methylene chloride data obtained for PEEK reinforced with continuous carbon fibres are provided for comparison to the neat polymer results.

(Keywords: polyetheretherketone; solvent resistance; fluid environmental effects; solvent-induced crystallization; plasticization)

INTRODUCTION

High-performance carbon fibre reinforced composites are becoming increasingly attractive for use in light-weight structural applications. Thermosetting matrices are typically used in these materials today. Although these composites have excellent specific mechanical properties which offer weight reductions, these properties decline dramatically in the presence of aggressive environments, particularly hot/wet conditions. Until now thermoplastics have not been widely used as matrix materials in high performance composites because of poor solvent resistance and failure to maintain adequate strength and stiffness at elevated temperatures. However, recently introduced high performance thermoplastic matrices could overcome these problems and bring additional desirable qualities, such as optimum processing characteristics and toughness improvements, for load bearing composite parts. A thermoplastic that has attracted interest in recent years as a matrix material for composites is polyetheretherketone (PEEK), whose repeat unit is:
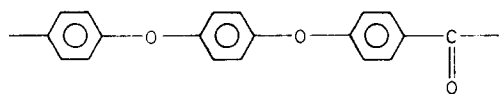
This aromatic semicrystalline polymer exhibits significant chemical resistance and elevated temperature performance[1-3]. As in other semicrystalline polymers the properties of PEEK depend upon the degree of crystal-linity as well as the different ways the crystalline and noncrystalline regions of the polymer can arrange. This internal structure, in turn, is the result of the thermal, mechanical, and environmental history of the polymer[4,5]. Before the potential of thermoplastic-based composites like PEEK/graphite can be fully realized, the processing–structure–property relationships for the neat polymer will have to be examined. This information can, in turn, be used to better understand the composite behaviour. Although this initial investigation focuses on the neat polymer in film form, preliminary data on single ply PEEK reinforced with continuous carbon fibres are also presented here to provide direct observation of the neat polymer behaviour in the composite.

EXPERIMENTAL

Our starting neat polymer was a low crystallinity PEEK film with a crystal volume fraction $V_x = 0.076$. Available under the trade name Victrex PEEK (Imperial Chemical Industries (ICI)); it will be referred to as PEEK1. In order to obtain film samples of higher crystallinity a series of annealing experiments were performed on PEEK1 to produce such samples. The annealing temperature was set between 230°C and 248°C, depending on the desired crystallinity, and was maintained for 10 min before the samples were allowed to cool slowly to room temperature. For this process the PEEK1 film was sandwiched between Kapton lined steel plates, and a moderate pressure was applied with clamps to prevent curling of the film. In general, PEEK can adhere strongly to mould surfaces,

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which can damage the film samples on removal from the mould. It was found that PEEK did not adhere to Kapton film so the mould release problems were avoided. The film sample annealed at 248°C had the highest volume fraction crystallinity ($V_x = 0.258$) and it will be referred to as PEEK2. Finally, PEEK reinforced with continuous carbon fibres, available under the trade name APC 1 from ICI, was also examined in this study for comparison, although it should be emphasized that the molecular structure and morphology of the polymer in the composite may be substantially different from the film samples.

Samples from the PEEK1 and PEEK2 films used in sorption–desorption experiments with different fluids were of size 8.0 cm × 1.6 cm × 0.006 cm. Culture tubes of size 20 mm × 140 m × 0.006 cm were filled with the specific fluid which had been preheated to the desired temperature. The film samples were immersed in the fluids and the tubes were corked. Water baths maintained the desired temperatures during the experiments. The fluids were deionized water, methylene chloride, and low density aviation hydraulic test fluid (Skydrol) manufactured by Monsanto. These fluids were chosen to represent a range of chemically aggressive environments that a high performance composite airplane part may naturally encounter.

To evaluate the effect of temperature on the sorption and resulting properties, film samples were immersed in the fluids at two different temperatures. The water and Skydrol were kept at 20°C and 70°C, while methylene chloride was kept at 20°C and 36°C because of its low boiling point. The 20°C and 70°C temperatures were preferred to allow comparison with work previously performed in our laboratory with other matrix polymers[6]. Samples immersed in the fluids were weighed on an analytical balance by removing them from the fluid, blotting carefully twice with filter paper, and pulling them through a folded tissue under light pressure to remove any residual surface fluid.

One set of samples was desorbed after it had approached apparent equilibrium in the fluids. The desorption was carried out at room temperature under vacuum (0.11 Torr). Samples for desorption were placed in fresh culture tubes which were put in a vacuum desiccator. The samples in the process of desorption did not require the blotting procedure for weight determination.

Density measurements on all films were made with a standard density gradient column prepared from aqueous solutions of calcium nitrate, giving a range of density between 1.2200 g cm^{-3} to 1.4000 g cm^{-3}.[7]

Thermomechanical (t.m.a.) and differential scanning calorimetric (d.s.c.) experiments were also conducted on the PEEK samples using a DuPont 1090 Thermal Analyzer attached to a 943 Thermomechanical Analyzer module and a 910 Differential Scanning Calorimeter. The t.m.a. module was equipped with a film tension probe and each run was performed under the same conditions; 1.4 mm sample length, 5°C min^{-1} heating rate, and a static load of 3 g. For samples that were tested after exposure to the fluid environments 30 min were allowed between removal of the sample from the fluid and the cooldown before the run. The d.s.c. scans were also performed at 5°C min^{-1}. The samples were cut with a holepunch which was 0.635 cm in diameter, giving maximum contact with the d.s.c. sample pan of the same diameter.

Finally, dynamic mechanical measurements were obtained with a Rheovibron DDV-II using previously developed techniques and environmental chamber improvements[8]. The sample size for these experiments was 6.0 × 0.4 cm, while the heating rate was 1°C min^{-1}. For the APC 1 composite sample the DuPont DMA 982 attached to the 1090 Thermal Analyzer was used, providing data in flexure.

RESULTS AND DISCUSSION

Density of annealed PEEK films

The crystallization kinetics for the PEEK polymer, as reported in detail by previous investigators, provided a half-time to maximum crystallinity of approximately 0.1 min[1] in the temperature range considered in this work[-1]. Therefore it was assumed that by maintaining the sample for a 10 min interval at a given temperature, equilibrium crystallization will be approached. The per cent crystallinities of films processed at different temperatures were calculated from density measurements and the published phase densities[1] by the following expression:

$$V_x = (\rho - \rho_{nx})/(\rho_x - \rho_{nx}) \qquad (1)$$

where

V_x = volume fraction crystallinity
ρ = measured density
ρ_x = density of crystalline phase = 1.4006 g cm^{-3}
ρ_{nx} = density of noncrystalline phase = 1.2626 g cm^{-3}

Table 1 lists the densities of the annealed films and, as expected, it shows that the per cent crystallinity increases monotonically with the temperature employed in making a given sample.

Sorption

Figure 1 shows the sorption of the fluids as a function of the square root of time for PEEK1. It can be seen that the sorption of water is slight and there is little sorption of Skydrol. However, methylene chloride is swiftly absorbed by the polymer and to a much larger extent. The apparent equilibrium weight-gain values from *Figure 1* are given in *Table 2*. It should be noted that the methylene chloride sorption values should only be considered approximate since even at room temperature methylene chloride desorbs and evaporates rapidly, and consequently the sample weight when exposed to methylene chloride is a function of time out of the fluid. Thus the weight-gain of the samples becomes a function of the specific weighing procedure that is utilized. Accordingly, the weighing procedure was standardized to give consistent results and required 50 s to perform. Because of this brief removal of the samples from the fluid, it may be assumed the weighing process did not interfere with the sorption.

Table 1 Density results for annealed PEEK1 samples

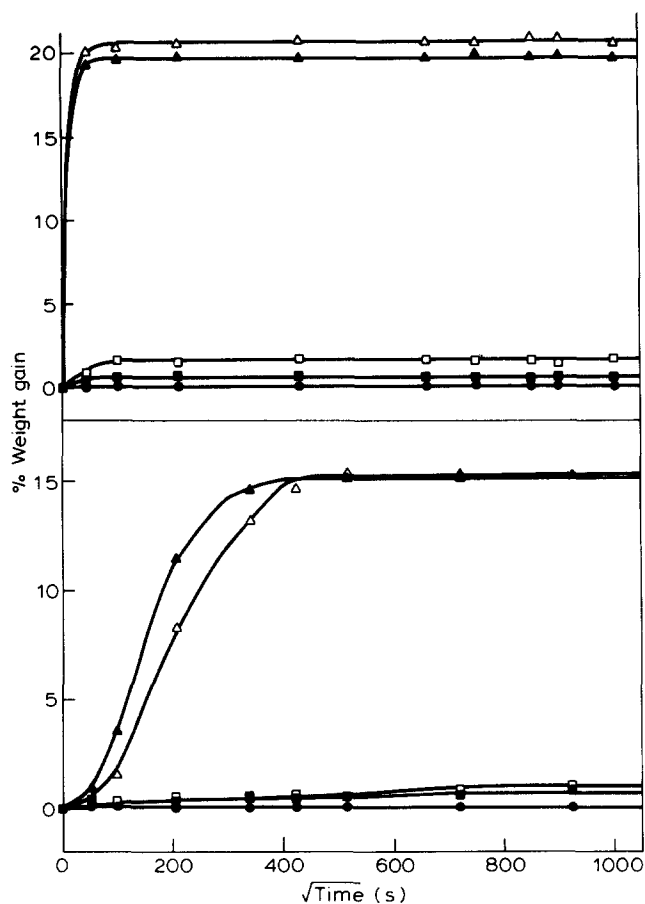| Sample	Crystallization temperature	Density (g cm^{-3})	Crystal volume fraction
PEEK1	–	1.2731	0.076
1	230° C	1.2927	0.218
2	235	1.2952	0.236
3	243	1.2962	0.243
4	241	1.2960	0.242
PEEK 2	248	1.2983	0.258

Figure 1 Sorption as a function of time for: a) the low crystallinity (7.6%) PEEK1 film exposed to different fluid enviroments, and b) the high crystallinity (25.8%) PEEK2 film exposed to different fluid enviroments. These enviroments were: ($\triangle$), methylene chloride at 20°C; ($\blacktriangle$), methylene chloride at 36°C; ($\square$), Skydrol at 70°C; ($\blacksquare$), Skydrol at 20°C; and ($\bullet$), water at 70°C and 20°C with essentially identical values

Table 2 Apparent equilibrium weight-gain for PEEK samples

Environmental treatment	% weight-gain	
	PEEK 1	PEEK 2
Water, at 20° C	0 0	0.1
Water, at 70° C	0.1	0.1
Skydrol, at 20° C	0.6	0.8
Skydrol, at 70° C	1.7	1.1
Methylene chloride, at 20° C	20.8	15.4
Methylene chloride, at 36° C	19.7	15.2

The sorption curves for PEEK2, the higher crystallinity sample, appear in *Figure 1* and the apparent equilibrium weight-gain values are given in *Table 2*. For these samples the higher level of crystallinity decreases the sorption of methylene chloride at both 20°C and 36°C. The weight-gain values in the other fluids are essentially unchanged from the PEEK1 values. The sorption kinetics are also slowed to an extent such that differences can be seen between the sorption of methylene chloride at the two temperatures. As expected, the higher temperature results in faster sorption, and reflects an increase in the diffusivity constant with temperature[6,9].

From the sorption data it should be noted that higher temperatures correspond with higher equilibrium weight-gain levels of water and Skydrol, but lower levels for methylene chloride. The density data suggests that this is

due to solvent-induced additional crystallization, which results in higher crystallinity in the sample at a higher temperature. This additional crystallinity lowers the magnitude of the methylene chloride sorption. This effect is more pronounced with PEEK1, which has a lower initial crystal volume fraction. The large difference between PEEK1 sorption at 20°C and at 36°C is related to the corresponding difference in the density data. The PEEK2 sorption at the two temperatures has only a small difference, which is also reflected in the density values.

The sorption of methylene chloride by APC 1 closely parallels the PEEK2 sorption data in that the higher temperature leads to faster sorption but results in a lower magnitude of apparent equilibrium sorption. The presence of the carbon fibres decreases the amount of material available for sorption, therefore the lower level of sorption is expected. The actual sorption by the PEEK matrix can be estimated by first calculating the mass fraction PEEK in the composite by:

$$M_p = V_p \rho_p / [\rho_{cf} + V_p(\rho_{cf} - \rho_p)] \qquad (2)$$

where

M_p = mass fraction PEEK in APC 1
V_p = volume fraction PEEK in APC 1 = 0.48[10]
ρ_{cf} = density of carbon fibres = 1.79 g cm^{-3}
ρ_p = density of PEEK matrix

The density of the PEEK matrix has been estimated to be 1.3 g cm^{-3} through density gradient and d.s.c. analyses. Thus with equation (2) the calculated weight-gain values are 16.6% for methylene chloride at 20°C and 15.9% for methylene chloride at 36°C. These magnitudes correspond very well with the neat PEEK sorption data.

Desorption

The desorption curves for PEEK1 and PEEK2 are given in *Figure 3*. The rate of desorption is essentially independent of the crystallinity, as shown by the methylene chloride desorption half-times of 68 s$^{1/2}$ for PEEK1, and 71 s$^{1/2}$ for PEEK2. The residual levels of fluid in the films after desorption are given in *Table 3*. These values once again show no dependence on crystallinity. Some negative weight-gain values were observed after the fluid desorption. Although well within the
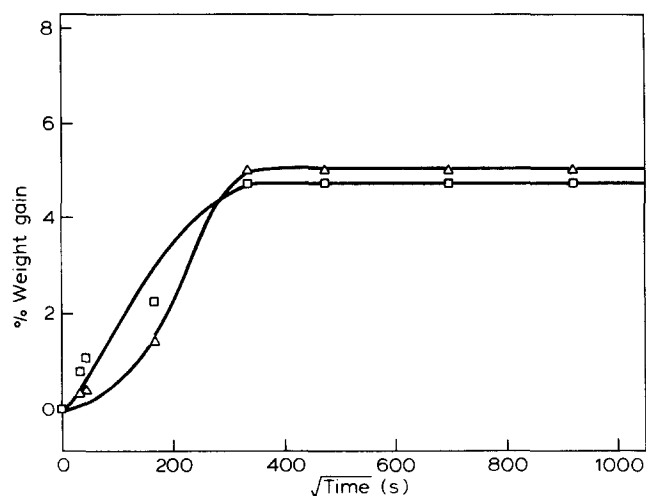

Figure 2 Sorption as a function of time for APC 1 single ply PEEK composite exposed to methylene chloride at two different temperatures: ($\triangle$), 20°C and ($\square$), 36°C
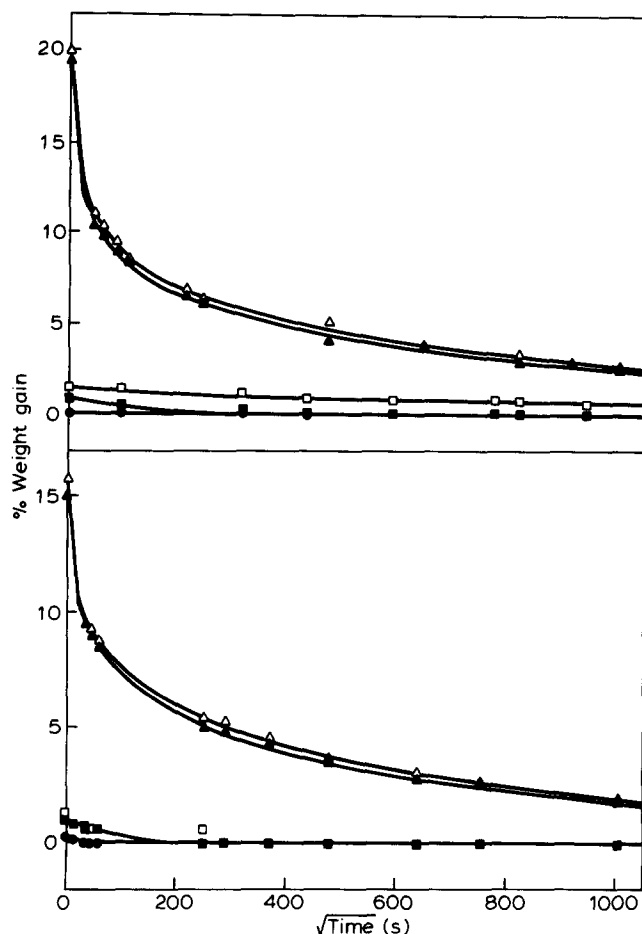
Figure 3 Desorption as a function of time for: a) the low crystallinity (7.6%) PEEK1 film exposed to different fluid enviroments, and b) the high crystallinity (25.8%) PEEK2 film exposed to different fluid enviroments. These enviroments were: ($\triangle$), methylene chloride at 20°C; ($\blacktriangle$), methylene chloride at 36°C; ($\square$), Skydrol at 70°C; ($\blacksquare$), Skydrol at 20°C; and ($\bullet$), water at 70°C and 20°C with essentially identical values

Table 3 Residual fluid levels after the desorption process

Environmental treatment	Residual fluid level	
	PEEK 1	PEEK 2
Water, at 20° C	±0.1%	±0.1%
Water, at 70° C	±0.1	±0.0
Skydrol, at 20° C	±0.1	±0.1
Skydrol, at 70° C	0.0	±0.1
Methylene chloride, at 20° C	1.1	1.1
Methylene chloride, at 36° C	1.1	0.8

accuracy of the data these negative values may be due to small amounts of water in the sample before the fluid exposures were begun and the initial sample weight measured. It should also be noted from the desorption data that the simple room temperature vacuum desorption which was used could not remove all of the methylene chloride from the film samples. The effect of this residual methylene chloride was apparent in the dynamic mechanical data obtained with these samples.

Density of fluid exposed samples

The densities of the PEEK materials after the fluid treatments are shown in *Table 4*. These densities are a combination of the density of the polymer and the density of the absorbed fluid. Assuming this combination can be

expressed by simple addition of the densities weighted with their respective volume fractions, the density of the PEEK after fluid treatment can be estimated as:

$$\rho_p = (\rho - \rho_f V_f)/V_p \qquad (3)$$

where

ρ = measured density
ρ_p = density of PEEK
ρ_f = density of fluid
V_p = volume fraction of PEEK polymer
V_f = volume fraction of fluid

Equation (1) was used to convert these calculated densities, ρ_p, into per cent crystallinities for the PEEK samples. The per cent crystallinities of the PEEK films after treatment with water or Skydrol were essentially unchanged from the values obtained before the fluid exposure. The films treated with methylene chloride showed a marked increase in crystallinity. Their calculated per cent crystallinities are shown with their densities in *Table 4*. This data shows the solvent-induced crystallization process reaches a higher extent of crystallinity at higher temperatures, and the previously low crystalline film PEEK1 is affected to a much higher degree. Thus, it is the lower level of crystallinity which causes the low temperature sample to absorb more methylene chloride than the high temperature sample.

Thermomechanical analysis

In general, thermomechanical scans show the dimensional change of the sample as a function of time and/or temperature and allow monitoring of the thermal expansion of the material. Polymer transitions of sufficient magnitude are detected by rapid variation in thermal expansion or contraction of the sample. PEEK undergoes a β transition near $-60°C$ (detected with dynamic mechanical experiments) but this transition is imperceptible in the t.m.a. scans. Indeed the data presented for the low crystalline PEEK film in *Figure 4* reveal the excellent dimensional stability of the PEEK polymer. The static load (3 g) imposed on the samples during the experiment causes the film to extend at the glass transition, which is shown by the small S-shaped shoulder at about 143°C. The larger transition observed at 169°C may be attributed to additional crystallization of the incompletely crystallized samples. It can be seen in *Figure 5* that these two transitions are suppressed by the presence of fluids in the

Table 4 Density (g cm^{-3}) of PEEK after environmental treatment. (Values in parentheses are % volume fraction crystallinities)

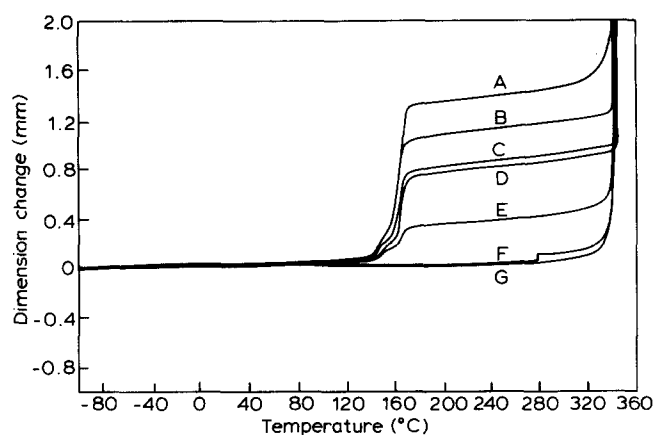| Environmental treatment	PEEK 1 after sorption	PEEK 1 after desorption	PEEK 2 after sorption
Water, at 20° C	1.2744	1.2736	1.3001
Water, at 70° C	1.2738	1.2738	1.2994
Skydrol, at 20° C	1.2743	1.2735	1.2984
Skydrol, at 70° C	1.2747	1.2733	1.2993
Methylene chloride, at 20° C	1.2961 (20.9%)	1.2899 (19.5%)	1.3109 (33.9%)
Methylene chloride, at 36° C	1.3104 (33.3%)	1.2982 (25.7%)	1.3141 (36.6%)

Figure 4 Thermomechanical data expressed as sample dimensional change as a function of temperature for PEEK1 samples: untreated PEEK1 (curve A), exposed to: water at 20°C (curve B), water at 70°C (curve C), Skydrol at 20°C (curve D), Skydrol at 70°C (curve E), methylene chloride at 36°C (curve F), and methylene chloride at 20°C (curve G)
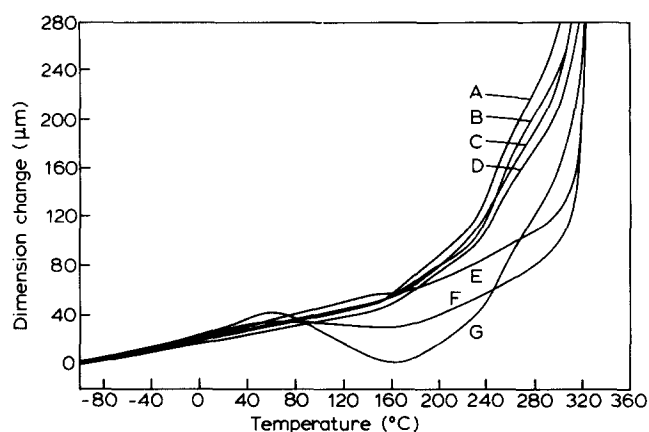

Figure 5 Thermomechanical data expressed as sample dimensional change as a function of temperature for PEEK2 samples: untreated PEEK2 (curve A), exposed to: water at 20°C (curve B), water at 70°C (curve C), Skydrol at 20°C (curve D), Skydrol at 36°C (curve E), methylene chloride at 36°C (curve F), and methylene chloride at 20°C (curve G)

matrix, and this suppression is in proportion to the amount of fluid absorbed by each sample. The samples treated with methylene chloride do not show either of these transitions. This could be due to the large quantity of absorbed methylene chloride or because of the accompanying additional crystallization.

The PEEK2 data shows that the transitions are substantially diminished with increasing crystallinity. The sorbed PEEK2 samples again showed the same transition suppression (*Figure 5*) but the magnitude of the transitions is also greatly decreased with the higher crystallinity. The dimensional stability of the higher crystallinity samples is now excellent up to the melting point of PEEK (340°C). There is also an additional transition near 250°C, which corresponds to the annealing temperature. This transition may be indicative of melting-recrystallization or relaxation of constraint chains in the noncrystalline regions and will be further discussed along with the d.s.c. results.

The 30 min period between removal from the fluid and the cooldown was to allow each sample a consistent time for ambient desorption. The desorption which could occur during the t.m.a. scan would be detected by shrinkage of the sample. This shrinkage is seen near the

glass transition in all of the samples treated with methylene chloride and Skydrol at high temperature, which suggests the possibility that fluids are retained in the matrix until the glass transition is approached.

Differential scanning calorimetry

D.s.c. scans measure the heat flow necessary to maintain whatever temperature program has been selected. Exothermic processes which occur during the scan appear as peaks on the graph. The area between the peak and a selected baseline can be integrated to give the energy per unit mass of the process. The choice of baseline can be difficult, and different methods have been suggested[11]. A simple linear baseline was selected for this study. Another problem is that the heat of fusion calculated by integrating the area under the curve at the melting point only indicates the state of the sample just prior to melting. Two processes which can occur before fusion are:

(1) crystallization of noncrystalline regions, giving rise to an additional peak and

(2) melting-recrystallization or relaxation of constraint chains in the noncrystalline region which occurs between the glass transition and the melting point of the polymer[12].

The first process is easy to correct by subtracting the heat of additional crystallization from the heat of fusion. The second process is difficult to account for quantitatively and remains a source of error in the interpretation of the d.s.c. data. Thus an independent method to correlate the d.s.c. results to crystallinity should also be employed as was done with the density gradient results in this study.

Figure 6 shows the d.s.c. curves for PEEK1 and PEEK2. The glass transitions were 144°C for PEEK1 and, upon magnification of the ordinate, 157°C for PEEK2, which reveals a strong dependence of the glass transition temperature on crystallinity. The PEEK1 glass transition compares well with the t.m.a. glass transition and, as in the t.m.a. data, there is a transition near 250°C for PEEK2. This is due to the fact that the degree of crystallinity which is possible to achieve below 250°C was already attained when the film was annealed. Therefore the melting-recrystallization and relaxation of the noncrystalline region processes can only start after the annealing temperature has been exceeded.

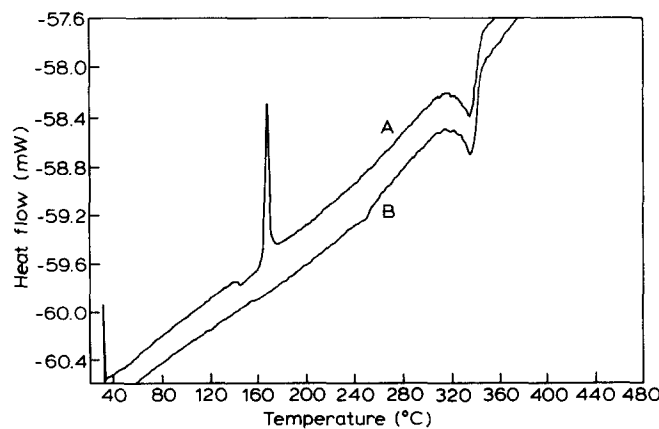The per cent crystallinity for PEEK1 and PEEK2 may be calculated from the data as:

Figure 6 D.s.c. scans for PEEK1 (curve A) and PEEK2 (curve B) obtained at 5°C min⁻¹

$$M_x = (H_m - H_c)/H_x \qquad (4)$$

where

M_x = mass fraction crystallinity
H_m = heat of fusion at T_m measured as the area under the d.s.c. melting peak
H_c = heat of additional crystallization, measured as the area under the d.s.c. crystallization peak
H_x = heat of fusion of crystalline material = $130 \, \text{J g}^{-1}$

For comparison with the crystallinity values from the density gradient column these figures need to be converted to volume fraction crystallinity according to the relation:

$$V_x = M_x \rho_{nx} / [\rho_x - M_x(\rho_x - \rho_{nx})] \qquad (5)$$

where the variables have been previously defined. The volume fraction crystallinities measured by the two techniques were found to be equivalent. Specifically, the values for PEEK1 and PEEK2 by density gradient column technique were 7.5% and 25.8%, respectively, as is shown in *Table 1*. When calculated from the d.s.c. data and equations (4) and (5), they were 8.8% and 22.3%, giving good comparison for the two techniques.

Dynamic mechanical

The dynamic mechanical data (presented here in terms of elastic modulus and tan δ) show that PEEK undergoes two transitions. As can be seen in *Figure 7* there is a broad transition which occurs around $-60°C$ (β transition) and
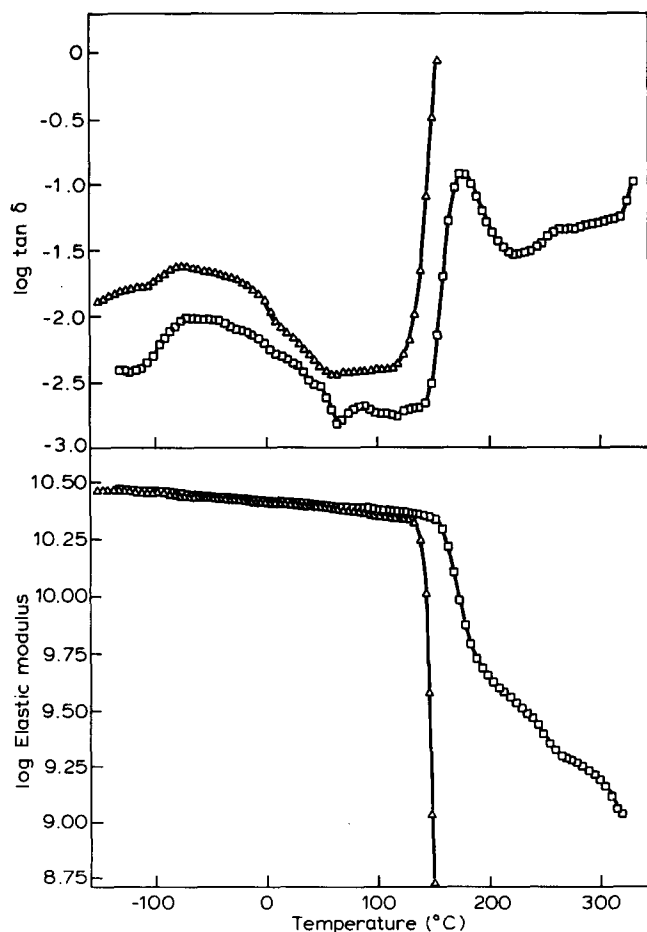

Figure 7 Dynamic mechanical properties measured in tension with the Rheovibron as a function of temperatures at 11 Hz for (△) PEEK1 and (□) PEEK2 films: a) tan δ, and b) elastic modulus
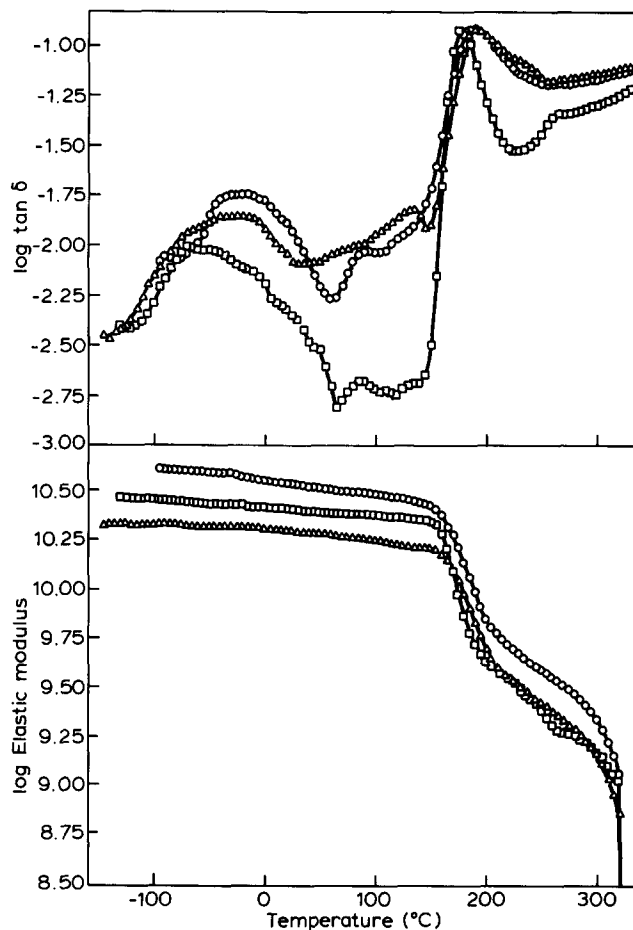

Figure 8 Dynamic mechanical properties measured in tension with the Rheovibron as a function of temperature at 11 Hz for different PEEK films showing the effects of crystallinity and fluid exposure: (□), a 25.8% crystalline PEEK2 film; (△), and originally 7.6% crystalline PEEK film after 20°C sorption in methylene chloride; (O), and originally 7.6% crystalline PEEK1 film after 20°C sorption and desorption of methylene chloride. Tan δ (a) and elastic modulus (b) curves are shown

the glass transition around 155°C (α transition). The elastic modulus is essentially unaffected by the β transition but falls rapidly at the α transition of the material.

Figure 7 shows the tan δ and elastic modulus curves as a function of temperature for PEEK1 and PEEK2 samples. The increase in crystallinity is reflected in the tan δ transitions being shifted to higher temperatures and becoming lower in magnitude. PEEK1 became very soft at the onset of the α transition and no further data could be measured. Data with PEEK2, as expected with its increased crystallinity, were collected past the α transition until the melting point was approached. It is interesting to note the strong dependence of the elastic modulus on the crystallinity at or above the α transition.

Finally, *Figure 8* shows the tan δ and elastic modulus curves for: (1) PEEK1 that has absorbed methylene chloride, (2) PEEK1 that has absorbed and desorbed methylene chloride, and (3) PEEK2. PEEK2 is used for comparison, as opposed to PEEK1, because PEEK2 is very close in crystallinity to the methylene chloride treated PEEK1 samples. Therefore the differences between the films are the absence or presence of methylene chloride, and the special morphological changes and/or additional crystallization caused by annealing or the specific fluid treatment. The presence of methylene chloride in the matrix shifts the tan δ transitions to higher

temperatures and increases the magnitude of the transitions. The higher baseline below the glass transition indicates that the plasticization effect, and hence the presence of methylene chloride, lasts until the glass transition (T_g). Because the boiling point of methylene chloride is 40°C and this effect continues up to 150°C, it can easily be hypothesized that the matrix can imprison a quantity of methylene chloride until the glass transition is attained. This supports the previously discussed t.m.a. data and the residual weight that was observed after the vacuum desorption of the samples.

The large amount of sorbed methylene chloride lowers the elastic modulus of PEEK, but upon desorption, the effect of the residual methylene chloride is overcome by the solvent-induced additional crystallization. As can be seen in *Figure 8(b)*, the elastic modulus is increased and is even greater than that of the higher crystalline sample PEEK2.

Finally, the dynamic mechanical data of the PEEK composite sample APC 1 is shown in *Figure 9*. It should be noted that the single ply was tested in flexure with the DuPont 982 DMA, thus assessing the matrix dominated properties of the composite. As can be seen, the observed behaviour is comparable to the data obtained for the higher crystallinity PEEK2 sample showing the α glass transition and the material's melting transition. This behaviour of APC 1 as well as its observed sorption behaviour in methylene chloride suggests that the PEEK in the composite may be analysed with morphological analogues of the neat polymer.

CONCLUSIONS

This study, as part of a broad development programme of processing–structure–property relationships for thermoplastic matrices in high performance composites, was focussed on PEEK polymer. Specifically, processing induced changes in crystallinity were examined by thermal and fluid exposure experiments and by examination of how these changes affected the thermomechanical bulk polymer properties.

Thermal annealing experiments on incompletely crystallized PEEK film samples demonstrated that increases in annealing temperature lead to increases in crystallinity and an apparent 'equilibrium' value. To our knowledge in
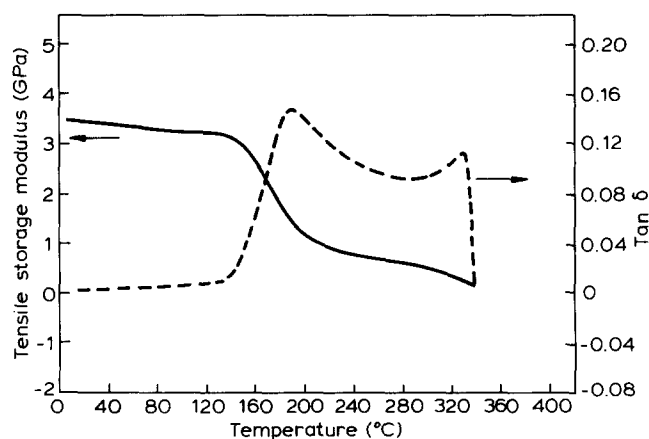
this study, for the first time it was observed that exposure of the incompletely crystallized PEEK film to methylene chloride both at 20°C and 36°C induced additional crystallization to occur in the samples leading to properties comparable to those obtained with the high temperature annealing experiments.

In general, PEEK proved to be highly resistant to water and hydraulic fluid (Skydrol), but large quantities of methylene chloride were absorbed by the polymer. The sorption experiments showed that the equilibrium fluid weight gain and sorption kinetics decreased with increasing the sample's crystallinity. Fluid temperature increases also led to increasing equilibrium weight gain sorption of water and Skydrol, but solvent-induced crystallization in methylene chloride reversed this behaviour with temperature. Similar trends were observed with the PEEK composite APC 1 when exposed to methylene chloride.

For both the low and higher crystallinity samples (PEEK1 and PEEK2), when methylene chloride was desorbed they exhibited similar desorption rate effects and final residual weights since they were of comparable level of crystallinity after their exposure to methylene chloride. In contrast, water and Skydrol desorbed completely and no residual weight of the fluid was detected.

Thermomechanical experiments (t.m.a.) on the different PEEK film samples confirmed the excellent, dimensional stability of the polymer. The sorbed samples exhibited a suppression of the glass and crystallization transitions that were observed in the t.m.a. thermograms of the original polymer. Further, this suppression was found to be related to the weight gain of the fluid absorbed by the sample. However, the t.m.a. results also revealed that these samples shrank as the glass transition temperature was approached during the run and the residual fluid desorbed.

The extent of crystallinity of all samples examined in this study was obtained by the density gradient column. Furthermore, a favourable comparison for crystallinities determined by d.s.c. and from the density gradient column technique was observed for the PEEK polymer.

Finally, dynamic mechanical experiments revealed two main viscoelastic transitions in tan δ for the PEEK polymer; an α or glass transition of the polymer at approximately 155°C and a secondary β transition at about -60°C. Comparison of PEEK samples with different crystallinities also demonstrated an established pattern in the dynamic mechanical spectrum for semi-crystalline polymers; namely, that increased crystallinity lowers the magnitude of the tan δ transitions and shifts the peak values to higher temperatures. Furthermore, the elastic modulus of PEEK was drastically increased with increases in crystallinity at or above the glass transition of the polymer. The dynamic mechanical data also showed that non-equilibrium crystallized samples of PEEK that were exposed to methylene chloride behaved like plasticized samples of higher crystallinity. This plasticization effect lasted far beyond the boiling point of methylene chloride and up to the onset of the polymer's glass transition. This suggested that only after sufficient mobility is reached during the glass transition can the crystallization inducing solvent, methylene chloride, be released.

A strong correlation of the dynamic mechanical transitions was observed with the neat polymer in tension and the d.m.a. of a single ply carbon fibre reinforced PEEK

Figure 9 Dynamic mechanical properties measured in flexure with the DuPont DMA as a function of temperature for an APC 1 single ply PEEK composite. Tan δ and elastic modulus curves are shown

composite APC 1 in flexure. These preliminary composite results along with the corresponding sorption experiments suggest that proper and careful application of processing–structure–property interrelations developed for the neat polymer may be extended to analyse and understand matrix dominated properties in the composite system.

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