Absorption of low-molecular-weight penetrants by poly(aryl ether ketone): 2. Bromoform

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The diffusion of bromoform vapour into amorphous and crystalline poly(aryl ether ketone) (PEEK) has been investigated from the increase in weight with time. The kinetics of diffusion into amorphous material follows case III diffusion, i.e. $w = kt^n$, where w is the fractional weight increase at time t and the n is 0.7. This is interpreted as plasticization by the bromoform followed by crystallization. Evidence for this mechanism can be seen in the changes in the dynamic mechanical thermal analysis of the materials. Desorption of the bromoform from the saturated material appears to follow case I with $n = 0.3$–0.4 rather than 0.5. Crystalline PEEK absorbs only 1% by weight of bromoform, and unlike the amorphous polymer this has no detectable effect on material properties.

(Keywords: poly(aryl ether ketone); amorphous; crystalline; diffusion; bromoform; chloroform; carbon fibre; composite; fracture toughness)

INTRODUCTION

In a previous paper[1] we have studied the diffusion of low-molecular-weight penetrants, such as chloroform and tetrahydrofuran, into amorphous poly(aryl ether ketone) (PEEK) and considered that the effects produced were consistent with plasticization of the polymer followed by crystallization. A well defined diffusion boundary existed between the rubbery swollen phase and the glass-like polymer, and this was associated with a sharp drop in penetrant concentration. Fickian diffusion was observed for the movement of this boundary with time, but there was a discontinuity in the diffusion constant at the boundary. Others[2] have reported the plasticization of PEEK and subsequent induced crystallization with methylene chloride.

Environmental stress cracking (e.s.c.) in amorphous PEEK can be observed with these crystallization-inducing low-molecular-weight penetrants, particularly if the polymer is strained to yield[1]. This could have significant effects in limiting the range of applicability of this material. Crystallinity in PEEK reduces the susceptibility to e.s.c. but does not eliminate it entirely.

In this paper the mechanism of diffusion of bromoform into amorphous PEEK and APC-2 carbon fibre composite has been studied as a function of sample thickness by the method of weight uptake and the change in mechanical response using dynamic mechanical thermal analysis.

EXPERIMENTAL

PEEK granules and the carbon fibre composites (APC-2) were supplied by ICI P&C plc. The granules were moulded, after drying *in vacuo* at 290 K for 16 h, into plaques $250 \times 250\ \mathrm{mm}^2 \times 1$ mm thick at 670 K, and subsequently stress relieved at the glass transition temperature. Sheets that were amorphous in their X-ray powder diffraction pattern, density and to d.s.c.[1] were obtained by quenching into ice/water. Crystalline material was obtained by slow cooling or annealing. The degree of crystallinity was determined by density or heat of fusion as measured by d.s.c., as outlined previously[1].

Bromoform was used as obtained from Hopkin and Williams Ltd, and chloroform from BDH Chemicals Ltd. Both were general-purpose reagents.

A Dynamic Mechanical Thermal Analyser, from Polymer Laboratory Ltd was used interfaced to an IBM microprocessor, System 2 model 30. Polymer samples were clamped and used in a flexing mode. Measurements of the flexing modulus E' and tan δ were made from 120 to 500 K, at a heating rate of 2 and 3 K min^{-1} and over the frequency range of 0.01 to 100 Hz, with mechanical displacements between 0.01 and 0.25 mm.

Differential scanning calorimetry was carried out on a Perkin-Elmer DSC model 2C, interfaced to an Apple 11GS microcomputer[3]. The calorimeter was calibrated from the m.p. of ultra-pure metals, indium, lead and zinc. A value of 28.45 J g^{-1} was used for the heat of fusion of indium.

Diffusion was measured from the increase in weight of thin films suspended in the vapour using a Perkin-Elmer

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Autobalance, AD-2, weighing to 2 μg. Increases in weight with time were recorded and displayed on a chart recorder. Measurements were made over 265 to 325 K.

Mechanical tests were carried out on an Instron Universal Testing Machine, floor model TT-BM, at cross-head speeds in the range 0.005–50 cm min^{-1}, and at a constant temperature and also in an environmental chamber. Fracture toughness was measured using single edge-notched specimens with the notch parallel to the fibre direction. This was considered to measure a matrix parameter. Flexural yield stress was measured using a three-point bend test, ASTM 790, with the fibres parallel to the breadth of the specimen. Accordingly it was considered to be dominated by the matrix properties.

RESULTS AND DISCUSSION

Diffusion studies

It has been observed previously[1] that amorphous PEEK absorbed up to 130% its own weight when suspended in bromoform over 2 days while the crystalline material absorbed very much less, about 0.9% over the same period. The progress of this diffusion of bromoform into amorphous PEEK was measured from the weight increase with time, using sheets of various thickness from 70 to 700 μm, and at various temperatures at constant film thickness (see *Figure 1*). An initial linear increase in weight was observed followed with a progressively decreasing uptake until the weight remained constant with time. This equilibrium was achieved, depending on temperature, after several days.

On equilibration, the reverse diffusion of the vapour from the polymer films into a nitrogen atmosphere was similarly followed from the loss in weight.

From Fick's second law for one-dimensional diffusion, a concentration gradient, $\partial c/\partial x$, will develop at time t at a point x along this axis, such that:

$$\partial c/\partial t = D\,\partial^2 c/\partial x^2 \qquad (1)$$

the diffusion constant D can be evaluated for the weight uptake in a plane sheet of thickness h, since in the initial stages of sorption and desorption studies:

$$W_t/W_e = (4D^{1/2}/\pi^{1/2}h)t^{1/2} \qquad (2)$$

where W_t and W_e are the weight increase at time t and finally at equilibrium. Plots of W_t/W_e against $t^{1/2}$ should be linear and the diffusion coefficient can be determined directly from the slope.

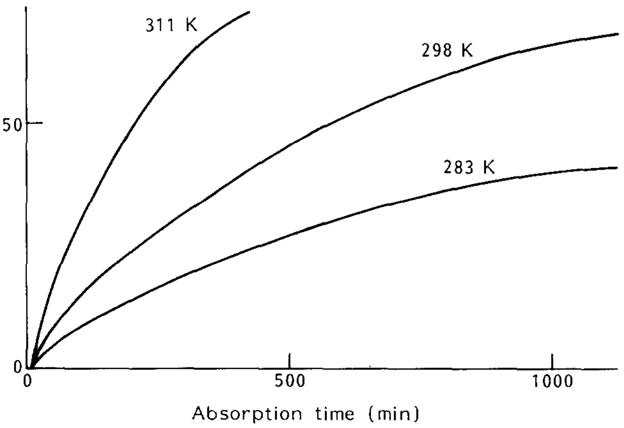

Figure 1 Weight increase with absorption of bromoform into amorphous PEEK: effect of temperature

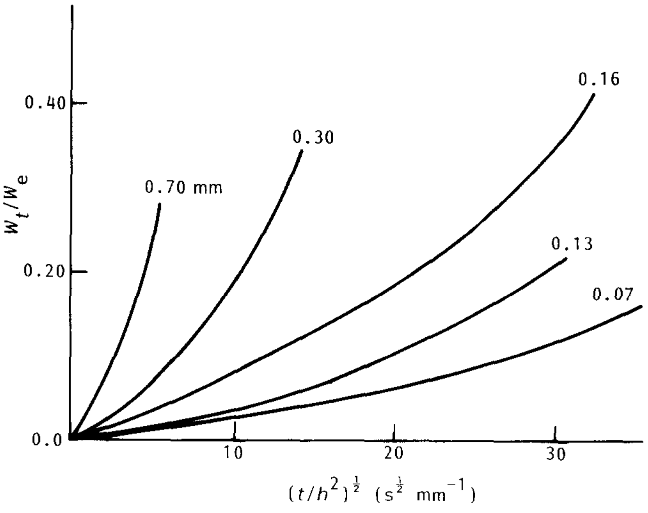

Figure 2 Diffusion of bromoform into amorphous PEEK: effect of sample thickness

Table 1 Diffusion characteristics of amorphous PEEK

(a) Absorption

Sample thickness, h (mm)	Diffusion coefficients		
	D (mm s$^{-1/2}$ × 10^6)	D' (s$^{-1/2}$ mm^{-1} × 10^4)	n parameter
0.07	3.5	7.1	0.76
0.13	15.2	8.1	0.76
0.16	19.6	7.7	0.72
0.30	82.5	9.2	0.66
0.70	237	4.8	0.74

(b) Weight loss

h (mm)	D (mm s$^{-1/2}$ × 10^6)	n
0.07	8.0	0.32
0.13	4.4	0.36
0.16	3.8	0.32
0.30	4.2	0.31
0.70	4.2	0.40

(c) Temperature dependence

Diffusion coefficient (mm s$^{-1/2}$)	Temperature (K)	Activation energy (kJ mol^{-1})
3.5	311	
1.5	297	900 ± 100
0.29	283	

With amorphous PEEK, the weight gained against $t^{1/2}$ exhibited marked upward curvature (see *Figure 2*), and this was particularly marked with the thicker specimens. Linearity was not observed except over a limited initial region, and the diffusion constant D, calculated from the initial slope and assuming that equation (2) was valid, was markedly dependent on sample thickness (see *Table 1*). It changed by two orders of magnitude for only one order change in film thickness. The parameter $D' = D/h^2$ was approximately constant, at about $(7 \pm 3) \times 10^{-4}$ s$^{-1/2}$ mm^{-1} (see *Table 2a*). Accordingly, it is apparent that Fickian diffusion is not a valid description of the weight uptake experiments and that from equation (2)

Table 2 Effect of immersion treatment on APC-2 composite sheet

(a) In bromoform

Sample crystallinity* (%)	Fracture toughness (MN m$^{-3/2}$)		Glass transition temperature, T_g (K)
	Treated	Untreated	
0	3.3 ± 0.7	5.7 ± 1.8	420 ± 2
11	5.9 ± 0.9	5.2 ± 1.8	431
11	7.8 ± 0.6	8.5 ± 2.7	432
13	5.1 ± 0.2	4.5 ± 2.0	432
17	5.8 ± 0.3	6.1 ± 2.1	431

*Crystallinity induced by cooling sample at different rates

(b) In various e.s.c. reagents

Liquid	Flexural yield stress (MPa)
Ethanol	62 ± 10
Bromoform	61 ± 8
25% H_2SO_4 aq.	64 ± 4
Chloroform	58 ± 10
Untreated	70 ± 9

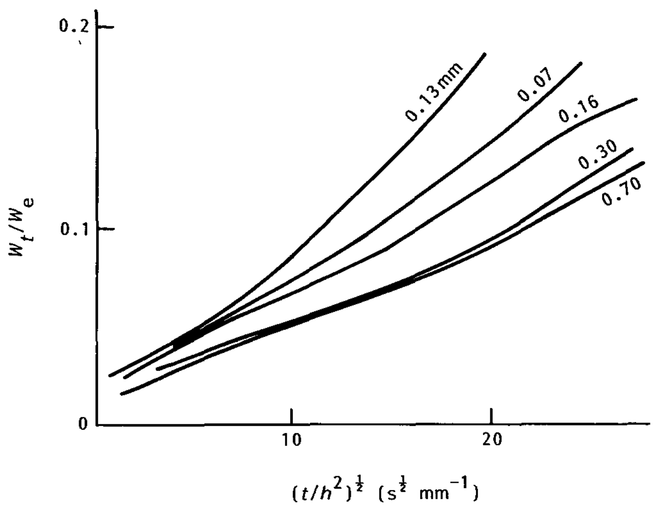

Figure 3 Desorption of bromoform: effect of thickness

the rate of uptake of vapour with the square root of time, i.e. $(1/W_e)(dW_t/dt^{1/2})$, must be independent of sample thickness.

However, similar plots for desorption (see *Figure 3*) exhibited only slight upward curvature and appeared to converge at zero time. Little or no variation of the diffusion constant D with sample thickness was observed, except for the 0.07 mm thick specimen, which appeared anomalous. The diffusion constant appeared to decrease to a minimum of $(4.0 \pm 0.2) \times 10^{-6}$ mm sec$^{-1/2}$ with the thicker specimens. This value was consistent with that obtained with the thinnest specimen in weight uptake studies, 3.5×10^{-6} mm s$^{-1/2}$, although the reverse dependence on thickness was observed (see *Figure 4*).

Diffusion of low-molecular-weight substances into glass-like polymers do not appear to obey Fick's laws of diffusion, while rubbers do. Low-molecular-weight additives will plasticize the thermoplastic and change the apparent diffusion constant as the mobility of the polymer molecules increase. Alfrey *et al.*[4] have proposed a useful classification according to the time dependence of diffusion and polymer relaxation, and distinguish between three types of diffusion:

(i) Case I obeys Fick's diffusion laws, and the rate of diffusion is much less than that of polymer relaxation.

(ii) Case II is the opposite in that diffusion is very rapid compared with the relaxation process.

(iii) Case III is non-Fickian and anomalous in that diffusion and relaxation rates are comparable.

In general, if w is the weight absorbed in time t, then:

$$w = kt^n \tag{3}$$

where k and n are constants. For case I, $n = \frac{1}{2}$; for case II, $n = 1$; and for case III, values lie between $\frac{1}{2}$ and 1 or change between the two values during the progress of the diffusion.

In terms of equation (3), plots of log w against log t were nearly linear (see *Figure 5*) for both absorption and desorption of bromoform. Film thickness had no great effect on the slopes of these plots but varied markedly for the two processes, i.e. $n = 0.73 \pm 0.05$ for absorption and 0.35 ± 0.05 for desorption (see *Table 1*).

Temperature had no effect on the diffusion mechanism in that the parameter n remained unchanged at 0.7 ± 0.1 over the range studied, 280–320 K. The apparent diffusion coefficient increased with temperature, and exhibited an apparent activation energy of 950 ± 50 kJ mol^{-1}.

The weight of bromoform taken up by crystalline PEEK and APC-2 with time can be seen in *Figure 6*, from which it is apparent that crystallinity greatly reduces the final amount of bromoform absorbed, presumably by it being confined to the amorphous regions. The mechanism of diffusion has altered, since n values of 0.2 and 0.3 were observed, respectively.

Dynamic mechanical properties

Tan δ and the flexural modulus E' for amorphous and crystalline PEEK are shown in *Figure 7* from 370 to 470 K. The first peak in tan δ in both samples corresponds with the glass transition temperature[5]. For the amorphous sample, the change in tan δ values associated with the glass transition is substantially higher, by about 4–5 times, and occurs some 10–20 K lower than the crystalline sample at 1 Hz. This is consistent with the reduced amorphous content and the restriction to chain mobility within the amorphous regions imposed by the presence of crystallites. From the shift in the observed glass transition temperature with frequency, activation

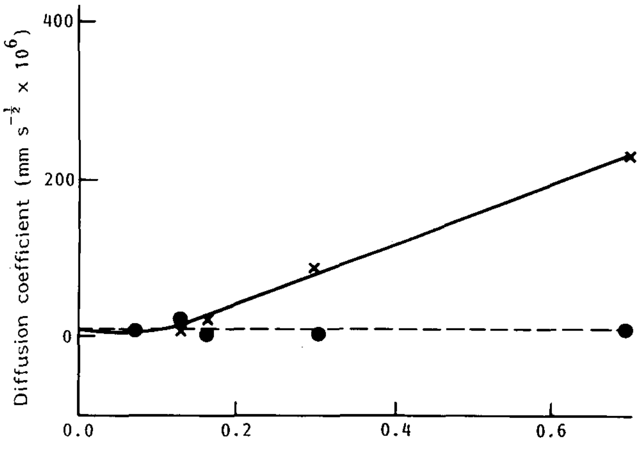

Figure 4 Thickness dependence of the diffusion coefficient: weight loss (●) and weight gain (×)

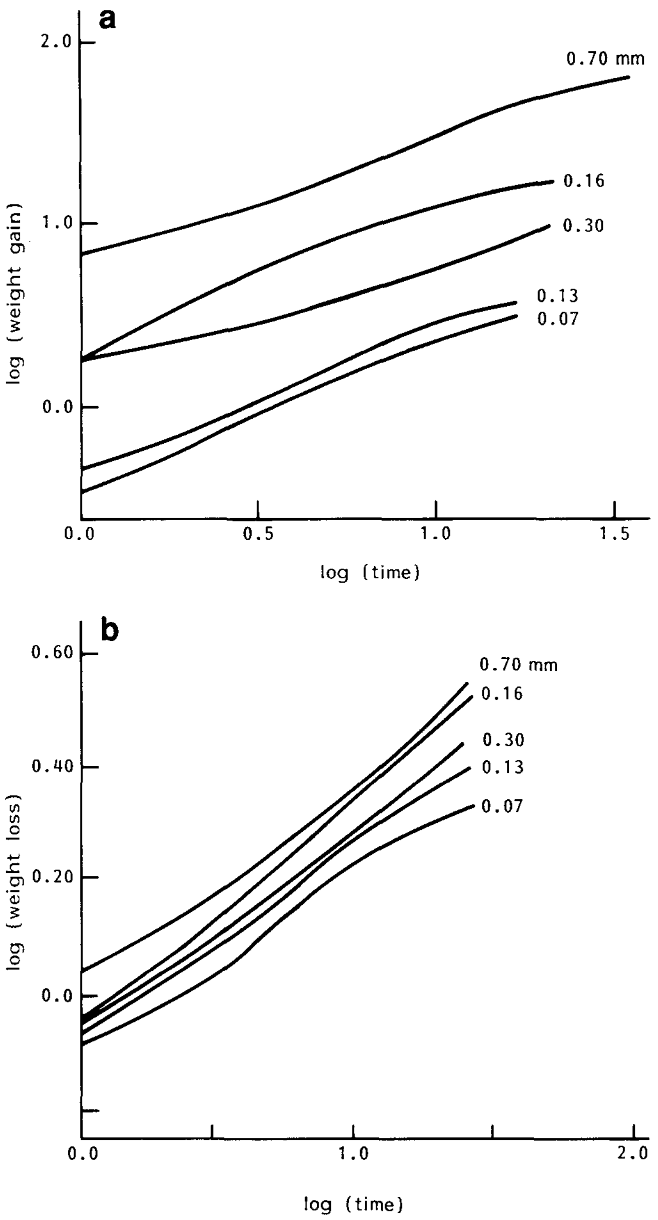

Figure 5 Log(weight) vs. log(time) plots: (a) absorption and (b) desorption of bromoform

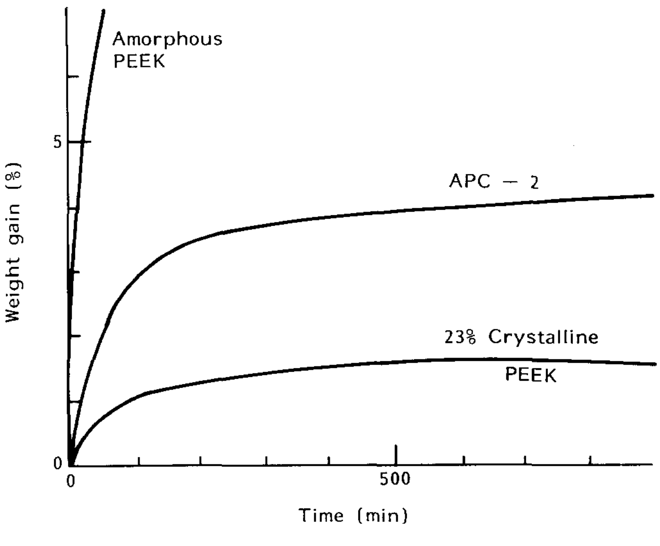

Figure 6 Comparison of the uptake of bromoform by amorphous PEEK, APC-2 and 23% crystalline PEEK

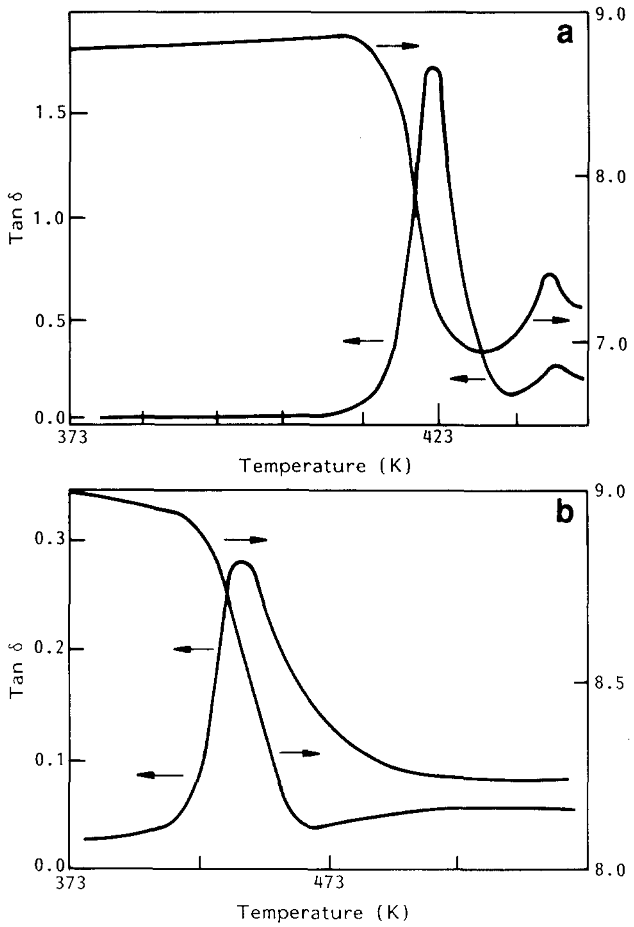

Figure 7 D.m.t.a. of PEEK at 1 Hz: variation of tan δ and E' with temperature for (a) amorphous and (b) crystalline PEEK

energies for the glass transition process of 1200 ± 100 and 900 ± 100 kJ mol^{-1} were obtained for the crystalline and amorphous material. The increase in tan δ and E' in the amorphous material above 530 K is associated with the onset of crystallization, as discussed previously[5].

Figure 8 shows tan δ as a function of temperature for amorphous PEEK that has been equilibrated in various liquids over 8 days. The glass transition as defined by the maximum in tan δ has shifted markedly to lower values, e.g. 310 K for bromoform. The untreated amorphous specimen has no comparable transitions below the glass transition region. Treatment with chloroform produces a similar effect but problems were encountered in that there was a continual loss of chloroform from the sample with rising temperature. This can be seen in the tan δ vs. temperature plot of a sample first heated to below the glass transition temperature, rapidly cooled and then examined by d.m.t.a. The glass transition temperature increased substantially but it was still lower than that of amorphous PEEK. On further heating above the glass transition temperature, tan δ again appears to increase due to the onset of further crystallization.

Accordingly the effect of the additives, chloroform and bromoform, is to plasticize the amorphous PEEK, lowering the glass transition, thus enabling crystallization to occur at an appreciable rate at ambient temperatures. The effect of conditioning in bromoform on the mechanical behaviour of PEEK was examined using single edge-notched specimens to determine their fracture toughness K_c (see *Table 2*). Specimens that were originally crystalline were basically unaltered by such

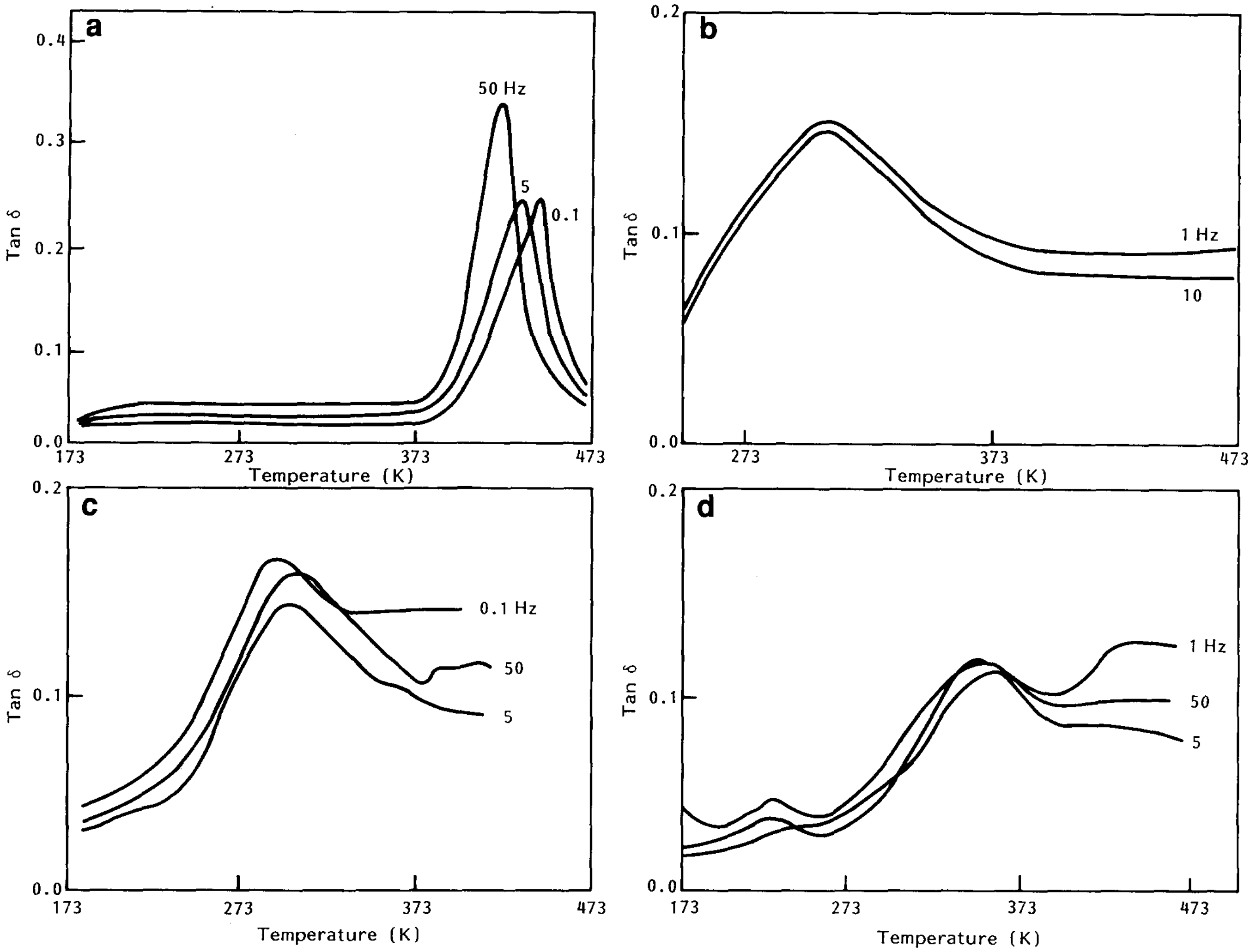

Figure 8 D.m.t.a. of immersed PEEK samples: variation of tan δ with temperature for (a) amorphous PEEK, (b) treated with bromoform, (c) treated with chloroform, and (d) after partial removal of chloroform by heating

treatment, with observable differences less than the experimental scatter. However, the amorphous material was substantially weakened, consistent with plasticization observed above.

APC-2 composite material, of carbon fibre/PEEK in which the PEEK matrix is substantially crystalline, was unaltered by immersion in various liquids for 8 days using the flexural yield stress as a guide. Immersion in bromoform also did not alter the fracture toughness. In studying these unidirectional composites, the notch was cut parallel to the fibre direction in order that the matrix alone should determine the failure mechanism.

CONCLUSIONS

Absorption of bromoform by amorphous PEEK follows case III diffusion and as the bromoform penetrates the matrix plasticization occurs accompanied by crystallization. The poorly crystalline material[1] produced desorbs bromoform following approximately case I diffusion, for which the Fickian diffusion coefficient is essentially constant. The plasticization that occurs substantially weakens the material in reducing the fracture toughness to one-half its original value.

The diffusion rate measured in terms of Fick's equation is independent of sample thickness D' of *Table 2*, and this is consistent with the sharp diffusion boundaries observed previously when PEEK samples were immersed directly in bromoform[1]. Diffusion is accompanied by the development of a crystallization front, and this severely limits the transfer of material across this boundary. It is also accompanied by a rapid change in D across the boundary and accounts for the presence of case III diffusion.

Crystalline PEEK absorbs not much more than 1–2% bromoform by weight, and this appears to follow a low power dependence on time, $n = 0.2$. While this small amount may plasticize the amorphous regions, it has no appreciable effect on mechanical properties, e.g. fracture toughness. Little or no difference was observed in the vapour uptake of the carbon-fibre-filled composites provided the matrix was crystalline, and there was little long-term effect of total immersion on mechanical properties.

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