Environmental stress crack resistance of and absorption of low-molecular-weight penetrants by poly(aryl ether ether ketone)

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(Received 13 March 1987; revised 16 October 1987; accepted 21 October 1987)

The diffusion of chloroform, bromoform, methylene chloride, α,α'-dichlorotoluene and tetrahydrofuran into amorphous poly(aryl ether ether ketone) (PEEK) has been investigated. Absorption of these liquids results in plasticization and crystallization of the polymer. The polymer–liquid interaction does not appear to involve hydrogen bonding to the carbonyl group of the polymer. A well defined boundary exists between the rubbery swollen phase and the glassy polymer, which is associated with a sharp drop in penetrant concentration. The boundary moves proportional to the exposure time to the power one-half, consistent with Fickian diffusion and a discontinuous change in the diffusion constant at the boundary. The environmental stress crack resistance of PEEK has been measured for a range of common organic solvents under constant stress and by application of the liquid as a measured drop directly onto the surface. The crazing stress could be measured from the minimum in the load.

(Keywords: poly(aryl ether ether ketone); crystallization; amorphous; diffusion; crazing; environmental stress cracking)

INTRODUCTION

Poly(aryl ether ether ketone) (PEEK) has a range of high-temperature properties that make it attractive as a speciality engineering polymer, particularly as a carbon-fibre-filled composite. Accordingly, there is considerable interest in its abilities to withstand aggressive environments and solvent attack, particularly environmental stress cracking. A recent publication has reported the plasticization of PEEK and subsequent induced crystallization by methylene chloride[1]. This could have a significant effect in limiting the range of applicability of this material, especially if similar effects are observed with partially crystallized material.

In this paper, the diffusivity of a range of liquids into amorphous PEEK is considered along with the influence of chemical structure of the penetrants, the kinetics of the diffusion process, and the penetrant concentration profile.

EXPERIMENTAL

As described previously[2], sheets, 1 mm thick, of both amorphous and 25% crystalline PEEK were moulded from commercial pellets as obtained from ICI plc. The melt viscosity of the PEEK was 0.43 kN s m^{-1} at a shear rate of 1000 s^{-1} and 670 K. Tensile properties were measured on a Minimat microscope extensometer (Polymer Laboratories Ltd) on dumbbell-shaped specimens cut from the moulded sheets. I.r. spectra were measured using a Nicolet Zeta MX1 *FT*i.r. spectrometer on 10 μm thick specimens moulded as above but between aluminium foil at 670 K and 40 MN m^{-2}, before quenching into ice/water and dissolving the foil in an aqueous solution of copper sulphate and sodium chloride. Wide-angle X-ray (WAXR) diffraction measurements were made with a Picker automatic diffractometer with a Cu Kα radiation[3]. Concentration profiles were measured using the X-ray analysis facility of the Cambridge Instruments S4 scanning electron microscope.

RESULTS AND DISCUSSION

Bulk diffusion studies

Slabs of amorphous PEEK, 1 mm thick by 3 × 1 cm, suspended in various organic liquids, were observed to swell as the liquid was progressively absorbed. Large quantities of the liquid, frequently in excess of the original weight, were taken up by the polymer. *Table 1* lists the percentage weight increase observed on exposing both amorphous and crystalline PEEK to various organic liquids, for 1 and 2 days respectively. Good penetrants appeared to require a hydrogen atom activated with an electronegative atom on the same carbon atom, i.e. $^{\delta+}\mathrm{H{-}C{\rightarrow}X}^{\delta-}$. Crystalline PEEK absorbed considerably less penetrant and not in proportion to the amorphous content. *Figure 1* shows the relative weight increase between amorphous and crystalline PEEK, when suspended in chloroform. They differ by two orders of magnitude. The uptake of chloroform completely altered the material properties of the amorphous PEEK, in swelling, decreasing its mechanical strength and making it opaque. On the other hand, it had little detectable effect on the mechanical properties or appearance of the crystalline material. This must clearly reflect the reduced mobility of the amorphous glass crosslinked by the crystallites.

From Fick's second law:

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

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0032-3861/88/040613-06$03.00

Table 1 Percentage weight increases after two immersion times, 24 h and 48 h

	Amorphous PEEK		Crystalline PEEK	
Liquid	24 h	48 h	24 h	48 h
Chloroform	55±5	55±5	0.4±0.1	1.0±0.1
Bromoform	120	130	0.6	0.9
Dichloroethane	40	60	0.6	1.0
Tetrahydrofuran	30	40	0.2	0.3
Carbon tetrachloride	0	0	0	0

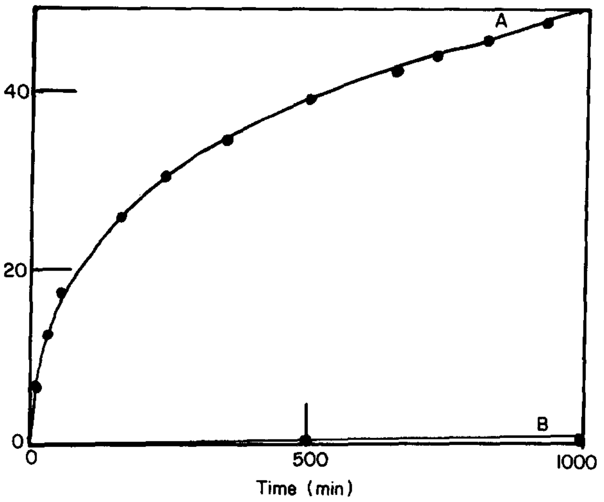

Figure 1 Weight increase in chloroform: curve A, amorphous PEEK; curve B, crystalline PEEK

relating concentration of diffusant c to time t and diffusion rate coefficient D, the total content of diffusant into a slab of thickness h at times t and ∞, w_t and w_∞, is:

$$w_t/w_\infty=(4/h)(Dt/\pi)^{1/2} \qquad (2)$$

A plot of w_t against $t^{1/2}$ for chloroform and amorphous PEEK was linear only after an initial period of 10 min (see *Figure 2*). The linear portion corresponded to a D value of about $1.0\times10^{-8}\,\mathrm{cm^2\,s^{-1}}$. The non-linear portion of the plot is consistent with considerable structural rearrangement of the PEEK, which followed the initial uptake of chloroform and the development of opaqueness and crystallinity.

Figure 3 shows the WAXR diffractograms of the amorphous PEEK on exposure to chloroform, indicating that it had crystallized to about 20%[3]. The diffusion of small molecules with induced crystallization has been observed in several polymer systems, and has been the subject of diffusion models proposed by Durning and Russel[4]. The crystalline reflections were extremely broad. This was considered consistent either with the presence of very small crystals or with little perfection within the crystals. The crystal structure was also clearly different to that observed previously[2] for PEEK crystallized isothermally above the glass transition temperature. Little differences were observed between the two crystalline samples in their i.r. spectra—thermally crystallized material exhibited additional absorptions over that of amorphous at 1117, 967, 849 and 845 cm^{-1}. The chloroform-induced crystallized material had these same absorptions, with others attributable to traces of chloroform. The intensities of the crystalline absorption were consistent with 25% crystallinity. Subtraction of chloroform absorption bands between 700 and 799 cm^{-1} from that of the treated sample produced negative absorption since the 757 cm^{-1} was broader in the liquid spectrum than in the presence of polymer. This is attributable to dilution rather than to specific polymer–solvent interactions. The carbonyl absorption band at 1652 cm^{-1} also did not change with conditioning in chloroform or crystallization, and there was no evidence of hydrogen bonding in the chloroform methine absorption band. Hydrogen bonding between chloroform and the carbonyl group was not present to any appreciable extent, unlike acetone/chloroform mixtures. Similar conclusions were reached from the i.r. spectra of PEEK crystallized in the presence of bromoform and dichloromethane.

Microscopic observation of diffusion

Immersed specimens were sectioned perpendicular to the slab thickness and examined in an SEM, without coating. They exhibited well defined boundaries between the swollen phase and the glassy polymer (see *Figure 4*). This boundary advanced linearly with the square root of the exposure time with all the liquids examined (see *Table 2*). The diffusion constant D could be determined from the concentration gradient, proportional to $D^{1/2}$. The values compared favourably with those determined from the weight uptake experiments. An activation energy for diffusion of bromoform was estimated to be 16±6 kJ mol^{-1} for bromoform. *Figure 4* shows the concentration profiles of the penetrants in a variety of sectioned specimens as determined using X-ray emission analysis. Loss of penetrant from the surface was

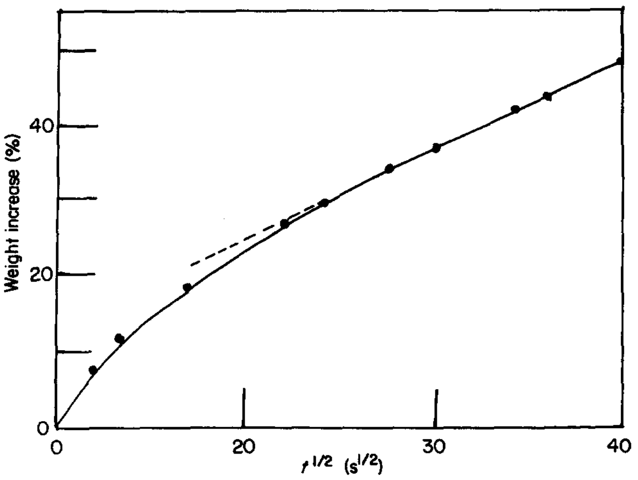

Figure 2 Diffusion of chloroform into amorphous PEEK

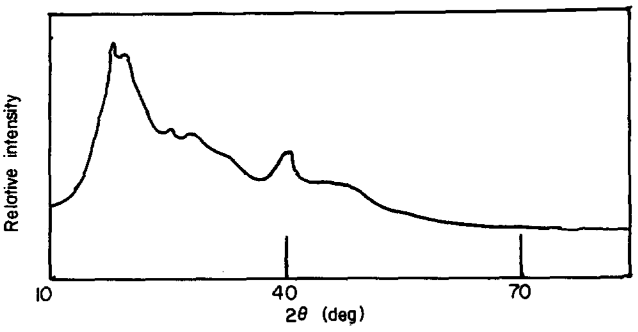

Figure 3 WAXR diffractogram of amorphous PEEK on exposure to chloroform

sufficiently low to enable the concentration profile to be determined accurately and reproducibly. Similar results were obtained by 'developing' the profile by exposing the concentration boundaries to silver nitrate in aqueous solution. The precipitated silver bromide or chloride could be determined by the X-ray emission lines on examination in the SEM.

The marked drop in concentration in the penetrant profiles (see *Figure 4*) corresponded to the visible boundary. The existence of such sharp boundaries is consistent with the results obtained by Durning and Russel[4] and with their model of a discontinuity in the diffusion coefficient at the boundary due to plasticization of the amorphous polymer and subsequent crystallization. The linear dependence of the position of the boundary on $t^{1/2}$ is characteristic of Fickian diffusion and consistent with the weight uptake experiments described above.

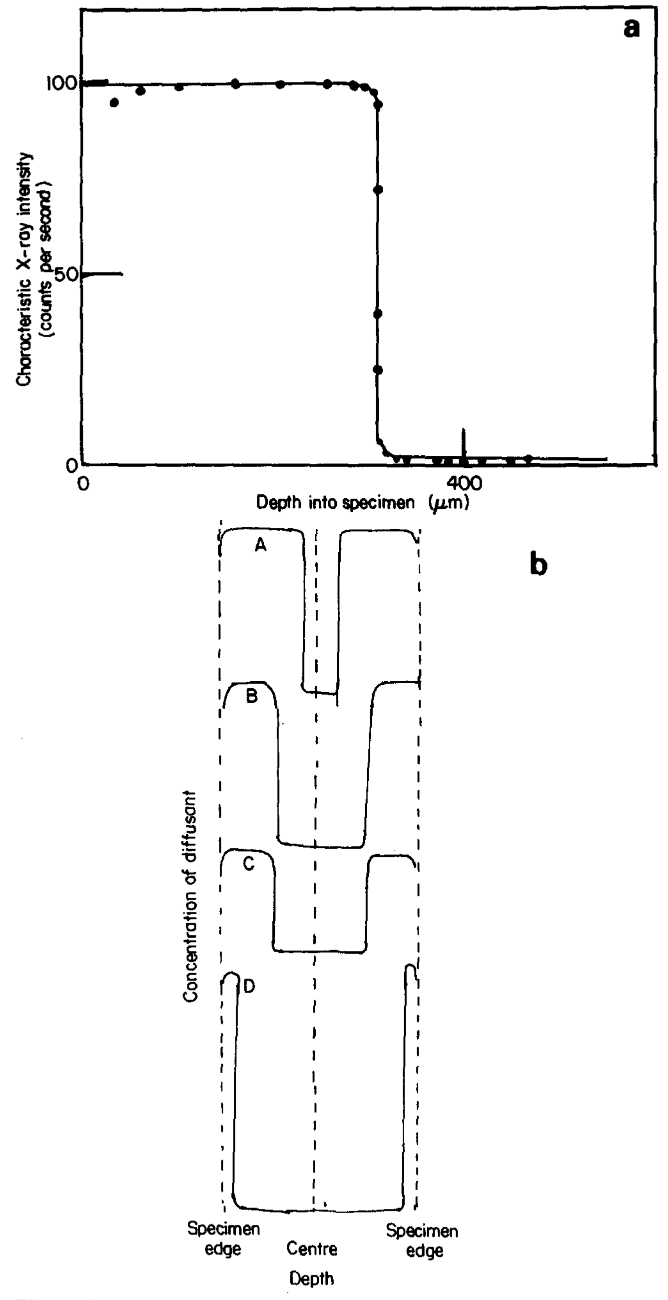

Figure 4 Penetration concentration gradients for PEEK at 293 K, 1 mm thick specimens. (a) Bromine concentration profile after diffusion of bromoform determined by the characteristic X-ray emission line. (b) Concentration profiles as in (a) for A, chloroform after 3 h; B, bromoform after 3 h; C, dichloromethane after 1 h; D, dichlorotoluene after 4 h

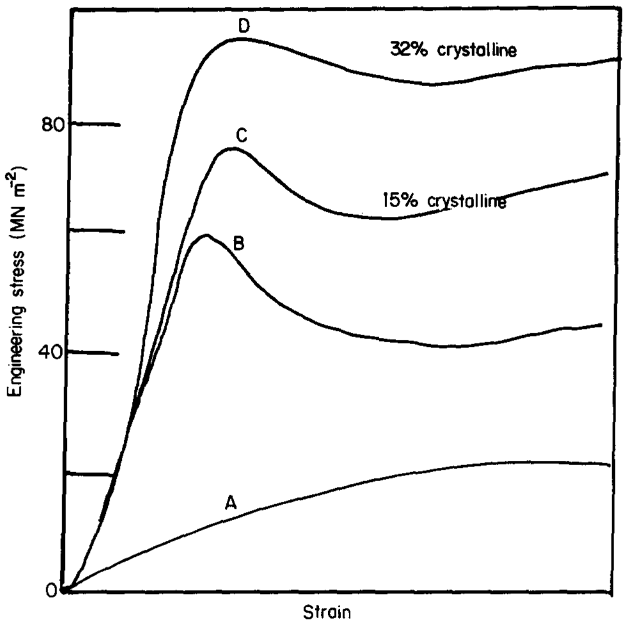

Figure 5 Tensile engineering stress–strain relationships: A, after exposure to chloroform; B, amorphous before exposure to chloroform; C and D, crystalline PEEK

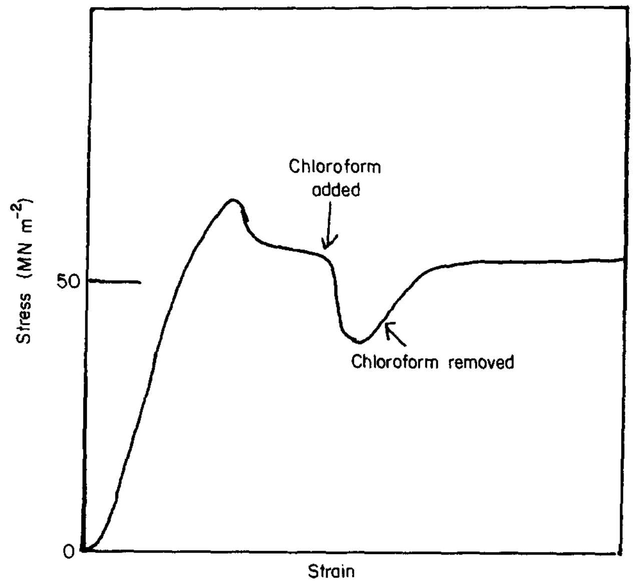

Figure 6 The effect of chloroform on drawing PEEK

Environmental stress cracking

The mechanical properties of the PEEK changed progressively on exposure to chloroform and the other liquids listed in *Table 1*. At low strain rates, amorphous PEEK deforms and fails in a ductile mode. Exposure to solvents decreased the tensile yield stress, and uniform drawing occurred rather than necking on yield. The overall effect was that of weakening the polymer substantially, of reducing the fracture energy, and was consistent with plasticization by the penetrants (see *Figure 5*).

The occurrence of environmental stress cracking[5,6] (ESC) was examined under constant stress by applying liquid directly to the surface of the undrawn region of a tensile specimen undergoing cold drawing. Addition of a standard drop of penetrant, 0.05 cm^3, caused a reproducible load drop and formation of crazes (see *Figure 6*). Different ESC agents produced load drops of different magnitudes but in proportion to the number and sizes of the crazes formed (see *Figure 7*). Chloroform was observed to be one of the more effective crazing agents, while carbon tetrachloride was one of the least[5]. Diluting the chloroform with carbon tetrachloride progressively reduced its effectiveness (see *Figure 8*), indicating that the size of the load drop was a measure of the susceptibility to ESC. Additional exposure of the stressed PEEK samples to the ESC agent did not increase the size of the load drop but only the time to recover to the drawing stress.

Accordingly, the load was considered to drop to the critical value required for craze formation. Both the load

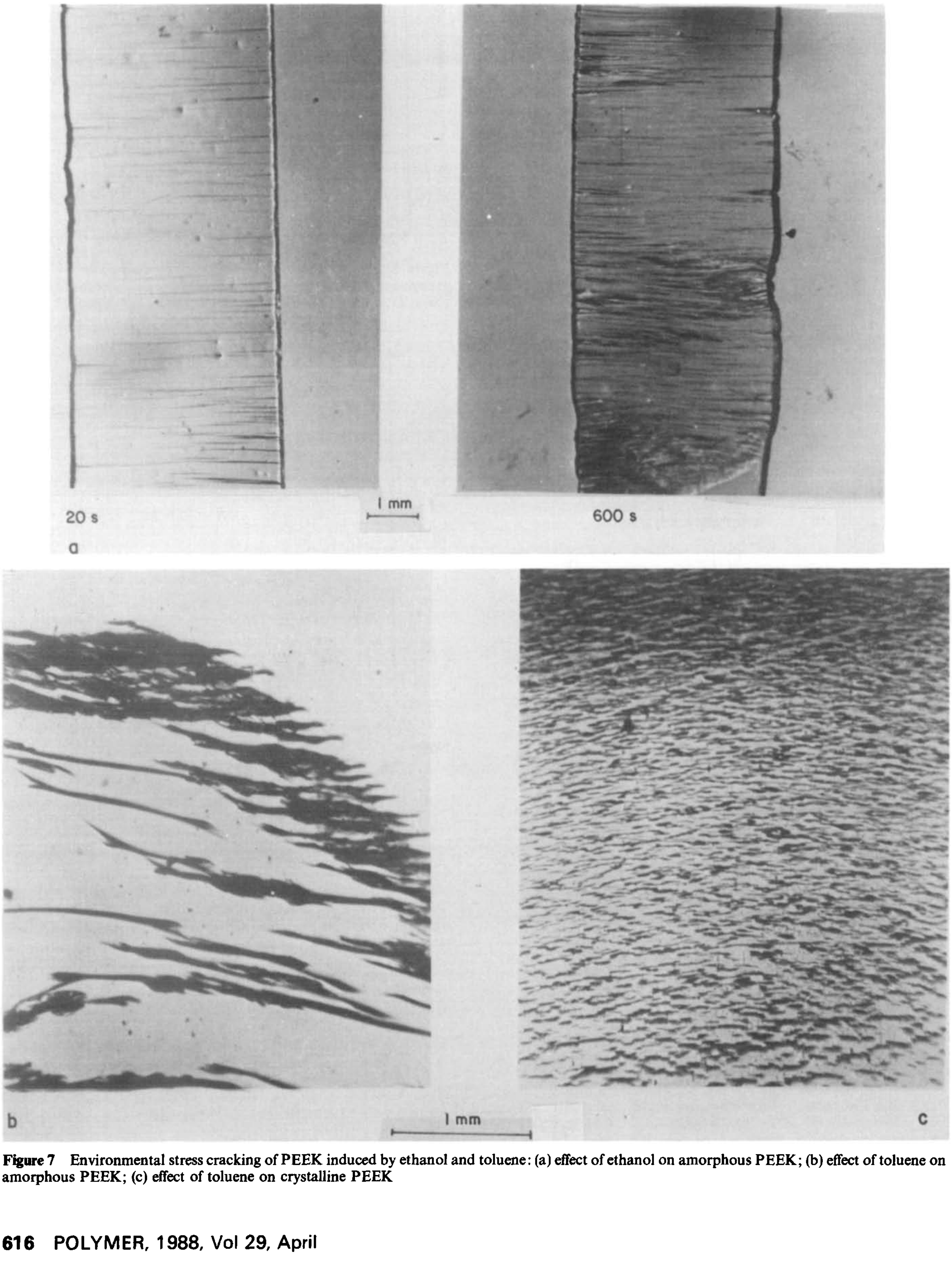

Figure 7 Environmental stress cracking of PEEK induced by ethanol and toluene: (a) effect of ethanol on amorphous PEEK; (b) effect of toluene on amorphous PEEK; (c) effect of toluene on crystalline PEEK

drop and the minimum load are a measure of ESC (see *Table 3*). On removing the ESC agent the load recovered, but the rate at which this occurred was proportional to the exposure time to the ESC agent. ***Figure 9*** shows the effect of exposure time on the load recovered 3 min after removal from the ESC agent, ethanol. The number and size of crazes increased progressively with exposure time.

Table 3 lists the load drops and the minimum loads obtained for a variety of ESC agents at a strain rate of $0.05\,s^{-1}$, and 0.13 mm thick specimens, for both amorphous and crystalline PEEK. The ranking order is the same for both polymers, although the size of the effect is not. The crazes in the crystalline polymer were substantially smaller in number and size than in amorphous PEEK, with higher crazing stresses.

There is a general trend in the ESC ability of a liquid and its solubility parameter δ, since it appears to reach a maximum at about $10\,cal^{1/2}\,cm^{-3/2}$ for both amorphous

Table 2 Diffusion gradients from movement concentration profiles

Liquid	Temperature (K)	Gradient ($cm\,s^{-1/2}$) $\times 10^3$	Diffusion coefficient ($cm^2\,s^{-1}$) $\times 10^8$
Bromoform	295	1.89±0.05	0.70±0.05
	310	1.89	0.70
	328	2.17	0.92
	351	2.90	1.65
	377	3.80	2.84
Chloroform	295	4.0±0.1	3.14±0.15
Dichloroethane	295	4.1	3.30
Phenyldichloromethane	295	0.4	0.031
Tetrahydrofuran	295	2.1	0.81

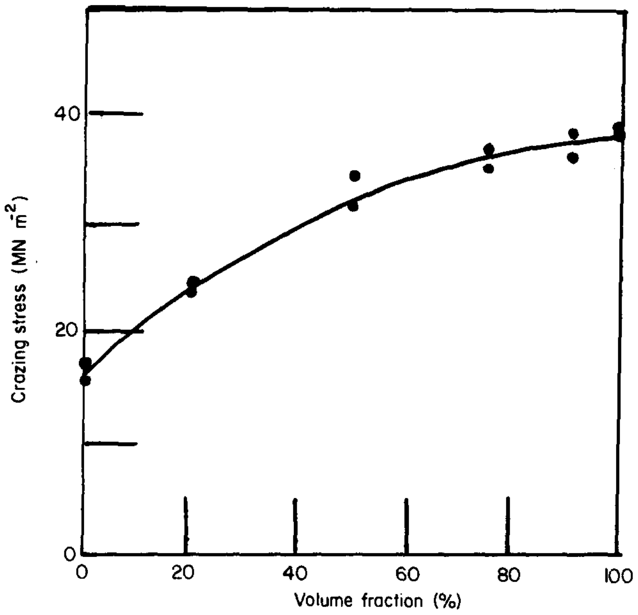

Figure 8 Effect of chloroform/carbon tetrachloride mixtures on the crazing stress. Volume fraction is chloroform in carbon tetrachloride

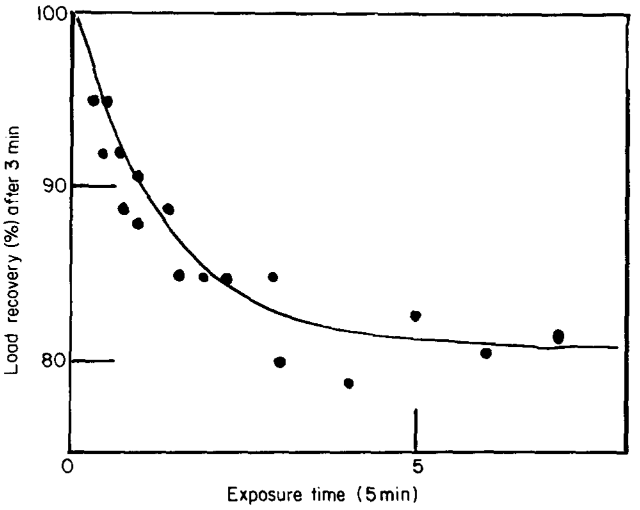

Figure 9 Percentage stress recovered after exposure to ethanol

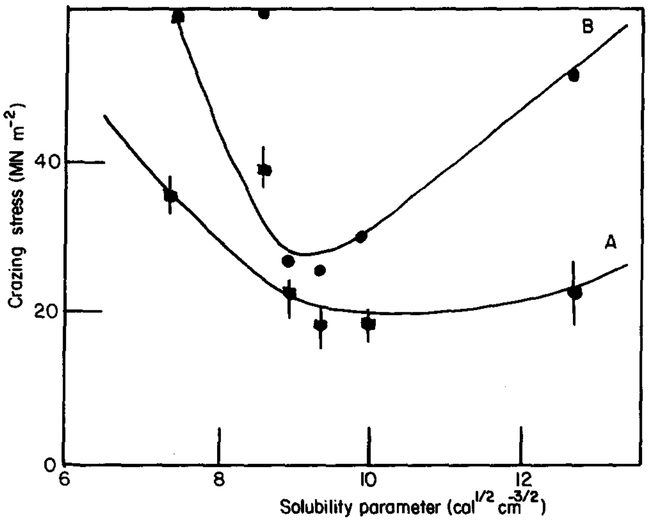

Figure 10 The effect of solubility parameter δ on the crazing stress: A, amorphous PEEK; B, crystalline PEEK

Table 3 Environmental stress crack resistance of PEEK

PEEK morphology	Agent	Solubility parameter ($cal^{1/2}\,cm^{-3/2}$)	Load drop (%)	Crazing stress ($MN\,m^{-2}$)
Amorphous	Petroleum ether	7.5	24.5±0.5	33.2±0.5
	Carbon tetrachloride	8.6	11.5±0.5	39.0±0.5
	Toluene	8.9	52.0±0.5	22.5±0.5
	Chloroform	9.3	60.0±2	17.5±1.0
	Acetone	9.9	57±8	18.8±1.0
	Ethanol	12.7	50±10	22.0±5.0
Crystalline	Petroleum ether	7.5	15±5	60±5
	Carbon tetrachloride	8.6	10±1	62±1
	Toluene	8.9	75±2	27±2
	Chloroform	9.3	65±10	25±5
	Acetone	9.9	33±5	30±5
	Ethanol	12.7	27±2	50±3

and crystalline PEEK (see *Figure 10* and *Table 3*). This is not only consistent with ESC being associated with partial dissolution, or plasticization, of the polymer but also with it being attributable to amorphous regions. On crystallization the ESC resistance improves, in that substantially higher crazing stresses are observed but the maximum crazing ability occurs at a similar solubility parameter to that of the amorphous polymer.

In both amorphous and crystalline PEEK, however, carbon tetrachloride did not fit into this pattern of behaviour, in being less effective an ESC agent than predicted from the solubility parameter. Diffusion studies also clearly indicate (*Tables 1* and *2*) that it does not appear to penetrate the polymer matrix to any appreciable extent. Other parameters are clearly important in determining ESC ability of the liquids.

Although crystallinity reduced the tendency for stress cracking to occur, it clearly did not eliminate it (*Figure 10*).

CONCLUSIONS

From the limited number of low-molecular-weight substances studied it would appear that those containing an activated hydrogen atom and an electronegative atom attached to the same carbon atom diffused most readily into PEEK and induced crystallization to a limited extent at room temperature. The rates of diffusion decreased with increasing molecular weight of the diffusant and reduced polarity. Similar studies on partially crystallized PEEK indicated that it was more resistant to the effects of the penetrants in changing the crystallinity, and diffusion is greatly reduced.

A well defined concentration gradient exists in the diffusion process, and this boundary diffuses into the bulk polymer proportional to the square root of the exposure time. This is consistent with Fickian diffusion. A discontinuous change in the diffusion constant at the interface between the semicrystalline and amorphous material must be present to account for the sharpness of the boundaries.

ESC in PEEK can be observed with most common solvents if it is strained to its yield stress. Exposure produces crazing and a drop to the crazing stress, which is characteristic of the ESC agent but appears to increase with solubility parameter consistent with a solubility parameter for PEEK about 10–11 $\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$. Carbon tetrachloride did not fit into this general pattern. Crystallinity in PEEK reduces ESC but does not eliminate it entirely.

ACKNOWLEDGEMENTS

DJK wishes to thank the SERC and International Paints Ltd, Felling, for the award of a studentship during the tenure of this work.

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