Solubility, diffusion and swelling of fluids in thermoplastic resin systems*

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The transport of liquids into semicrystalline thermoplastic resins such as poly(aryl ether ether ketone) (PEEK) is an extremely complex process, markedly dependent upon the temperature, crystallinity and concentration of the penetrant at the surface. Similarities and differences in the sorption, desorption, resorption, swelling and solvent-induced crystallinity of toluene and carbon disulfide into amorphous and semicrystalline PEEK are reported. The transport of these two liquids into PEEK illustrates many of the complexities associated with non-Fickian diffusion: sharp penetration front, slow relaxation processes, solvent-induced crystallinity and anisotropic swelling and deswelling. Desorption is a two-step process in which 30–50% of the penetrant is rapidly desorbed in a few hours. The rate of CS_2 sorption and desorption is much greater than that of toluene. The rate of resorption is significantly less than that of the initial sorption but the desorption process is essentially unchanged.

(Keywords: PEEK; toluene; swelling; transport properties; carbon disulfide; solvent-induced crystallinity)

INTRODUCTION

The sorption and subsequent transport of liquids or vapours through an organic matrix is a complex phenomenon which consists of essentially two processes: solubility and diffusion. The general question of solubility is usually formulated in terms of a solubility parameter, in a manner similar to that originally proposed by Hildebrand, which is based on thermodynamic considerations (for example, see ref. 1). The rate of penetration, usually called diffusion, of the liquid (or vapour) into the solid matrix is normally described in terms of Fick's laws. Fick's first law (in one dimension) is usually written in terms of the flux (F) through a surface. The flux is proportional to the concentration gradient ($\partial c/\partial x$):

$$F = -D\frac{\partial c}{\partial x} \tag{1}$$

where D, the constant of proportionality, is the diffusion coefficient. Fick's second law relates the concentration change as a function of time to the change in flux with respect to position, thus, for unidirectional diffusion:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{2}$$

In the simplest case, the diffusion coefficient D is only a function of temperature and we have classical Fickian diffusion:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{3}$$

For a large flat surface at constant concentration with sorption only occurring in one dimension, solution of equation (3) leads to:

$$D = \frac{\pi l^2}{16}\left(\frac{S}{C_\infty}\right)^2 \tag{4}$$

where $2l$ is the thickness of the sample, C_∞ is the surface concentration (solubility) at the temperature of interest and S is the slope of the linear region of the curve, i.e. $\mathrm{d}C/\mathrm{d}t^{1/2}$ during the initial portion of the sorption process. (For an excellent discussion of the diffusion process, see ref. 2.) Thus, Fickian diffusion predicts that the penetrant is sorbed at a rate proportional to the square-root of time. Equation (4) can be rearranged to:

$$D = \frac{\pi}{16}\left[\frac{d\left(\frac{S}{C_\infty}\right)}{\frac{\mathrm{d}t^{1/2}}{l}}\right]^2 \tag{5}$$

When plotted in this manner, i.e. fractional weight gain (S/C_∞) as a function of square-root time divided by thickness, the diffusion coefficient is a normalized value, independent of thickness, and can be used for modelling samples of arbitrary thickness. A fundamental criterion for Fickian sorption is that surface concentration immediately attains its equilibrium value upon a change

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in conditions and remains constant throughout the sorption process, i.e. the polymer chain segments in the surface layers must 'instantaneously' equilibrate.

Fickian diffusion is rarely observed for the transport of a liquid through a glassy polymer, i.e. below the glass transition temperature, T_g. In most polymers, deviations from Fickian diffusion arise as a consequence of the finite rates by which changes in polymer structure occur in response to stresses imposed upon the material before and during the sorption–diffusion process. A general description of non-Fickian or anomalous diffusion process in glassy polymers was first characterized by Alfrey *et al.*[3]. Various forms of non-Fickian diffusion have been classified as case II sorption or super case II sorption. (For an excellent discussion of non-Fickian diffusion, see refs. 4 and 5.) The various types of diffusion can be defined in terms of the manner in which the sample sorbs the penetrant as a function of time. In general the fractional weight gain, M_t/M_∞, (where M_t is the mass sorbed after time t and M_∞ is the equilibrium value) can be expressed as:

$$\frac{M_t}{M_\infty} = kt^n \tag{6}$$

For planar geometry, if $n = \frac{1}{2}$, the diffusion is classified as Fickian or pseudo-Fickian if the other criteria for Fickian diffusion are not met; case II if $\frac{1}{2} < n < 1$; and super case II if $n > 1$. One of the characteristics usually observed in anomalous diffusion is that the penetrant advances through the resin as a sharp front rather than exhibiting a classical exponential-type profile. If the polymer is partially crystalline, the transport process is markedly dependent upon the degree of crystallinity as well as the temperature. In addition, the polymer may exhibit solvent- (or more appropriately penetrant-) induced crystallization (SIC) and show anisotropic swelling. All of the above phenomena have been observed in the sorption of toluene by the partially crystalline thermoplastic polymer, poly(aryl ether ether ketone) (PEEK).

PEEK is a material of particular interest for use in high performance composites. PEEK has a relatively high melting point (345°C), a T_g of approximately 145°C, and its crystallinity ranges from zero (amorphous) to about 40%, although its nominal degree of crystallinity is approximately 30%.

A large number of publications have described many properties of PEEK and numerous engineering reports have described the processing of PEEK composite. It is commercially available both in neat resin form and as composite (APC-2) from ICI Americas Inc. It is generally considered to be a stable inert material and has been described as 'insoluble in all common solvents'[6]. However, recent work has shown that several fluids, including methylene chloride, chloroform, carbon disulfide, benzene and toluene, are readily absorbed by and swell PEEK[7-15]. The equilibrium concentration of these fluids in amorphous PEEK ranges from 50 wt% for chloroform to 20 wt% for toluene and CS_2.

EXPERIMENTAL

Samples of films, 0.25 mm in thickness, of amorphous (< 1% crystallinity) Stabar K200 were obtained from ICI America (Wilmington, DE, USA). The films were annealed in a forced air oven for selected time intervals at approximately 160°C to obtain 15% crystalline PEEK. Higher crystallinity material (29%) was obtained directly from ICI (Stabar K300); this material is crystallized directly from the melt.

The degree of order (crystallinity, $\%C$) of the samples was determined from the measured density by using the relationship reported by Blundell and Osborn[16]: $\%C = 1015.4 - 1282.05/\rho$. The density was determined by the neutral buoyancy method using aqueous solutions of ferric chloride with specific gravities in the range of 1.26–1.36. Previous studies have shown that density measurements accurately reflect the crystallinity of samples prepared thermally but underestimate the amount of crystalline order in samples crystallized by SIC[15].

The liquids, toluene and carbon disulfide, were chromatographic grade and were used without further purification. Sorption was accomplished by immersing the samples in the liquid contained in 2.5 × 15 cm culture tubes which were placed in a thermostatted aluminium block. At appropriate intervals, the samples, whose dimensions were typically 4 × 1 × 0.025 cm, were removed from the culture tubes, blotted dry, and weighed on an analytical balance. Pseudo-diffusion coefficients were calculated from the linear region of the weight gain *versus* square-root time plots according to equation (4). Dimensional changes accompanying the sorption of the liquid by the PEEK film were measured. Thickness was determined in three places with precision calipers and averaged; width and length were determined with a precise ruler while being maintained in the flattened position. All dimensional changes are reported as relative values, i.e. percentage change, rather than as absolute values.

RESULTS AND DISCUSSION

The transport of liquids into a thermoplastic polymer such as PEEK below its T_g is a complex process that can conveniently be divided into three separate phenomena: (1) sorption and swelling; (2) desorption and deswelling; and (3) morphological changes such as SIC which accompany the transport process. The latter process, i.e. SIC, has a profound effect upon both the sorption and desorption process.

We noted in earlier publications that the rate of penetration of toluene into PEEK was a strong function of both temperature and crystallinity[14]. In fact, we found that in 29% crystalline PEEK at 35°C the induction period for the sorption process to begin was greater than 1200 h, even when the sample was immersed in toluene at 35°C. For all intents and purposes the 29% crystalline material appeared to be impervious to toluene at 35°C but a 0.25 mm thick amorphous material reached saturation[13] (19 wt%) in approximately 18 h. However, PEEK with intermediate crystallinities, up to 18.8%, was found to sorb toluene but exhibited an induction period which was a strong function of both temperature and crystallinity. At 35°C the induction period for toluene sorption in 11.5% crystalline PEEK was greater than 4900 h; it increased with the fourth power of the crystallinity and decreased with temperature with an apparent activation energy of 50 kcal mol^{-1}.

CS_2 is also readily absorbed by PEEK; in fact, amorphous PEEK also sorbs approximately 19 wt% CS_2 at 35°C. Although the rate of penetration of CS_2 into crystalline PEEK is significantly slower than in the amorphous material, CS$_2$ readily penetrates crystalline PEEK even at 35°C.

Sorption and swelling

Gravimetric sorption/desorption curves showing the accompanying swelling changes in all three principal directions for the transport of toluene into 29% crystalline PEEK are shown in *Figure 1*. The sorption was conducted at 80°C while the toluene was desorbed at 95°C. The data are shown as a function of square-root time in order to best visualize all parts of the sorption/desorption process in a single figure. The weight gain curve exhibits a short induction period followed by a region of relatively slow weight gain which is linear with square-root time and finally a period of rapid weight gain. This curve illustrates that even highly crystalline PEEK absorbs a significant quantity of toluene. The curve can be conveniently divided into four separate regions: (1) the initial uptake; (2) an equilibrium or plateau region; (3) a rapid desorption region within the first hour of desorption; and (4) a slow desorption region of several thousand hours.

Typical sorption/desorption curves showing the weight gain and swelling for CS$_2$ into amorphous and 29% crystalline PEEK are shown in *Figures 2* and *3*, respectively. Note that CS$_2$ reached saturation in approximately 100 h (10 h$^{1/2}$) while toluene required more than 600 h (25 h$^{1/2}$) even though the toluene sorption was conducted at 80°C and the CS$_2$ sorption at 35°C. The sorption of CS$_2$ into the amorphous material is quite similar to that observed for toluene, except that CS$_2$ is completely desorbed after 60 h and toluene is not completely desorbed after many hundreds of hours.

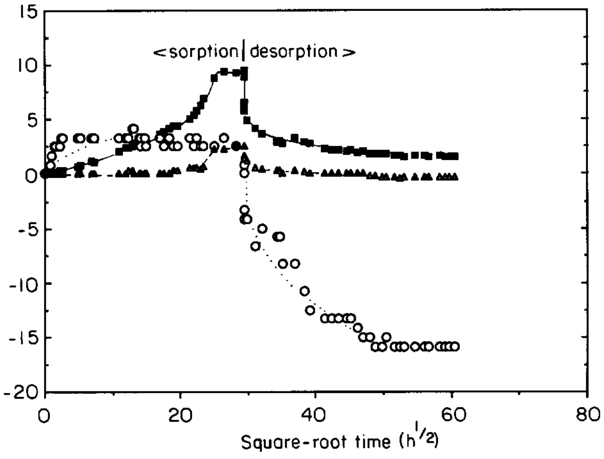

Figure 1 Weight changes and swelling during sorption (80°C)/desorption (95°C) of toluene from 29% crystalline PEEK: ■, weight; ○, thickness; △, length

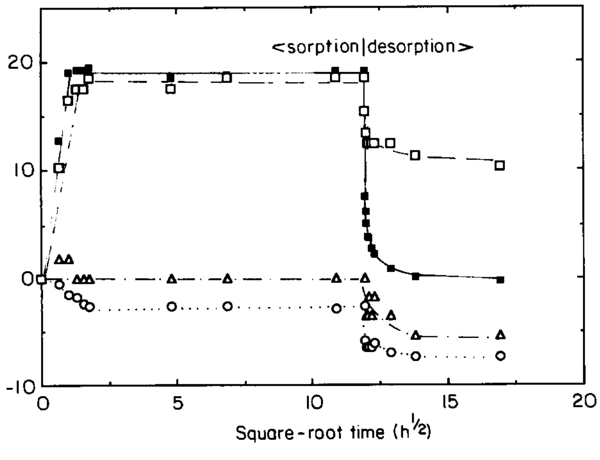

Figure 2 Weight changes and swelling during sorption (35°C)/desorption (95°C) of CS$_2$ in amorphous PEEK: ■, weight; ○, length; △, width; □, thickness

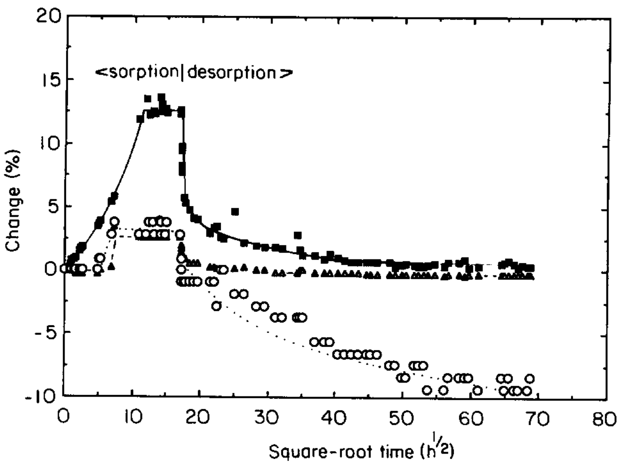

Figure 3 Weight changes and swelling during sorption (35°C)/desorption (95°C) of CS$_2$ from 29% crystalline PEEK: ■, weight; △, length; ○, thickness

The rate of penetration is determined from the slope of the linear region of the sorption curve and represents the rate at which the sharp boundary between the swollen and pristine region moves through the resin. Pseudo-diffusion coefficients are determined from the slope of the linear region and the solubility using equation (4). At 35°C in amorphous PEEK the rate of penetration of CS$_2$ is almost five times greater than that for toluene and the pseudo-diffusion coefficients differ by a factor of 20. The difference is even greater in the 29% crystalline material, where the penetration rates shown in *Table 1* differ by only a factor of three, but the toluene data are for a sample immersed at 80°C compared to the CS$_2$ data at 35°C. The sorption of toluene into 29% crystalline PEEK at 35°C is so slow that it is difficult to measure, and based on earlier measurements, we can estimate an induction period of greater than 300 000 h! The difference in the penetration rate and pseudo-diffusion coefficient of CS$_2$ into 15 and 29% crystalline PEEK is small and different to that observed for toluene.

Although the rates of penetration of CS$_2$ and toluene are quite different, their swelling characteristics are similar. Both liquids produce anisotropic swelling which, for the amorphous material, is primarily confined to the thickness direction (toluene swelling of amorphous PEEK is shown in Figure 6 in ref. 14). The results are summarized in *Table 2* where the crystallinity, maximum weight gain, i.e. solubility ($W_{\max}$), maximum thickness increase ($\Delta T_{\max}$), maximum volume change (based on dimensional changes, $\Delta V_{\max}$), and theoretical volume change (based on the mass of liquid sorbed divided by its density, ΔV_T) are given. Both liquids are sorbed to approximately the same degree, i.e. 19 wt% in amorphous PEEK, 13–15 wt% in 15% crystalline PEEK, and 9–12 wt% in the 29% crystalline material. However, the mole fraction or number of molecules sorbed per monomeric unit of amorphous phase is different; these results are shown in *Table 3*. (The number of molecules

Table 1 Penetration and diffusion of liquids into PEEK

Liquid	Initial crystallinity, X (%)	Temperature (°C)	Penetration (wt% $h^{-1/2}$)	Surface concentration, C_∞ (wt%)	Proportionality constant, D ($\times 10^{-12}$ $m^2 s^{-1}$)
CS_2	0	35	19.0	19.4	3.38
CS_2	15	35	1.08	15.6	0.017
CS_2	29	35	0.78	12.4	0.013
Toluene	0	35	4.1	19.2	0.16
Toluene	15	65	0.96	13.4	0.018
Toluene	29	80	0.26	9.3	0.003

Table 2 Dimensional changes (swelling) accompanying the sorption of liquids in PEEK[a]

Liquid	Crystallinity[b] (%)	W_{max} (%)	ΔT_{max} (%)	ΔV_{max} (%)	ΔV_T (%)
CS_2[c]	Amorphous	19.4 ± 1.0	22.1 ± 0.7	19.4	16.7 ± 1.7
CS_2	15	15.6	13.3	15.8	17
CS_2[c]	29	12.4 ± 0.05	5.2 ± 0.3	12.7	8.8 ± 1.0
Toluene	Amorphous	19.2	24.5	28.0	21
Toluene	15	13.4	16	20	18
Toluene	29	9.3	2	13.9	3

[a] See text for explanation of symbols

[b] Based on density

[c] Values are average (standard deviation) of four separate analyses

Table 3 Mole fraction of liquid absorbed per monomeric unit of amorphous PEEK

	PEEK crystallinity		
Liquid	0	15%	29%
CS_2	0.73	0.70	0.66
Toluene	0.60	0.49	0.41

sorbed per molecule of amorphous phase is determined from the relationship:

$$\left\{\frac{\left[\frac{W_{max}}{100}\right]}{MW_l}\right\} \div \left\{\left[\frac{1}{MW_p}\right]\left[\frac{100-X}{100}\right]\right\} \qquad (7)$$

where W_{max} is the maximum weight gain, MW_l and MW_p are the molecular weights of the liquid and PEEK monomer (288), respectively, and X is the initial crystallinity of the sample.) CS_2 appears to be entirely absorbed in the amorphous region and the crystalline region has little or no effect upon the amount of CS_2 absorbed in the amorphous phase. However, crystallinity does reduce the amount of toluene which is sorbed by the amorphous region; for example, the amount of toluene expected in the 71% amorphous material (29% crystalline) is 13.6 wt% (19.2×0.71) but the amount oberved was only 9.3 wt%. Clearly, the crystalline regions of PEEK affect the amount of toluene that can enter the amorphous regions but have little or no effect upon the amount of CS_2 absorbed in these regions.

Amorphous and crystalline PEEK show marked differences in their swelling behaviour. The amorphous material swells anisotropically, the predominant swelling in the thickness direction (approximately 20%) accompanied by a small 2–3% decrease in length and no change in width. The deswelling, from the swollen rubbery state, is essentially isotropic with a 7, 6 and 6% decrease in thickness, length and width, respectively. This is similar to that observed during the deswelling of toluene from initially amorphous PEEK[14].

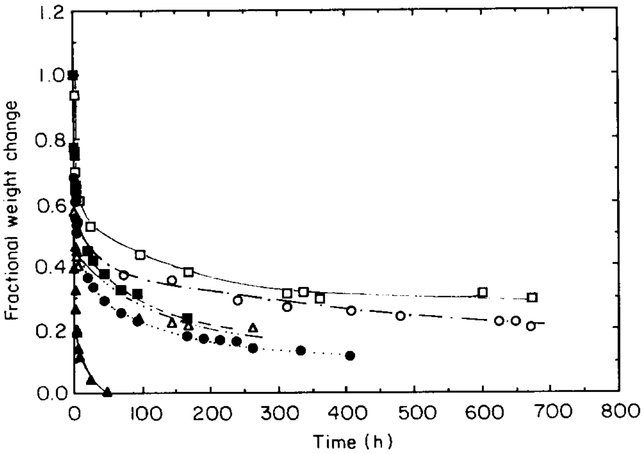

Figure 4 Fractional weight change at 95°C of toluene and CS_2 from swollen PEEK: □, toluene/29% crystalline PEEK; ○, toluene/15% crystalline PEEK; △, toluene/amorphous PEEK; ■, CS_2/29% crystalline PEEK; ●, CS_2/15% crystalline PEEK; ▲, CS_2/amorphous PEEK

The swelling phenomenon in the crystalline material is quite different than in the amorphous material. Both CS_2 and toluene show the same general features (see *Figures 1* and *3*): in the sorption phase, the thickness and length swell 2–3% with little change in width; during desorption the thickness decreases 10–15% and the length returns to its original value. Thus, deswelling from the swollen initially crystalline resin is highly anisotropic compared to the nearly isotropic deswelling observed from the initially amorphous resin.

Desorption

The normalized weight loss curves, i.e. fractional weight change, from the desorption (at 95°C) of CS_2 and toluene from initially amorphous, 15% crystalline and 29% crystalline PEEK, are shown in *Figure 4*. An expanded view of the first 25 h of the desorption processes is shown in *Figure 5* to illustrate the similarities in the early stages of desorption. Three features are readily apparent: (1) 40–60% of the fluid is rapidly desorbed in a few hours; (2) CS_2 completely desorbs from amorphous PEEK in about 60 h; and (3) toluene is held much more tenaciously than CS_2 and, even in the amorphous material, it is not readily desorbed. The primary reason for the fast and slow desorption regions results from the plasticization of the resin by the liquid. When in the swollen

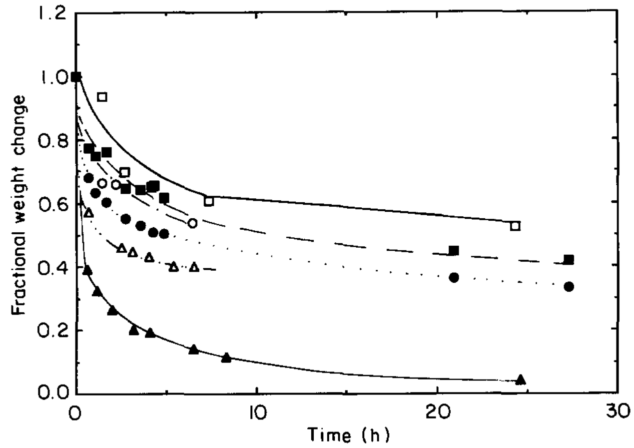

Figure 5 Expanded view of fractional weight change at 95°C of toluene and CS_2 from swollen PEEK: symbols as in *Figure 4*

rubbery state (high penetrant concentration) the liquid rapidly desorbs, but when the swollen resin loses sufficient penetrant it passes into the glassy region (low penetrant concentration) and desorption is very slow. The concentration of absorbed liquid required to yield a T_g equal to the temperature of the desorption chamber can be calculated from the equation described by Fox[17]:

$$\frac{1}{T_{g_R}} = \frac{W_p}{T_{g_p}} + \frac{W_l}{T_{g_l}} \qquad (8)$$

where T_{g_R}, T_{g_p} and T_{g_l} are the glass transition temperatures of the swollen resin, pure PEEK and liquid, respectively, and W_p and W_l are the weight fractions of the polymer and liquid, respectively. The amount of toluene required to yield a T_{g_R} equal to that of the desorption chamber (i.e. 95°C) is approximately 4.4 wt%. A similar calculation for CS_2 is more difficult since the T_g of CS_2 is not readily available, although it can be estimated to be between one-half and two-thirds of its melting point ($T_M = 164$K); therefore, T_g (CS_2) is between 82 and 109K. Thus, the amount of CS_2 required to yield a T_g of 95°C (the temperature of the desorption chamber) is 2.5–3.5 wt%, not significantly different to that of toluene, and we would expect to observe a second slow desorption region. Thus, either CS_2 has a different plasticizing effect on PEEK than does toluene or the molecular geometry of the molecule is sufficiently different that it can diffuse through the glassy state. We believe the latter is the case and the linear CS_2 molecule has a molecular diameter of approximately 3.3 Å compared to a minimum molecular dimension of greater than 4.0 Å for toluene.

Sorption/resorption

The weight and dimensional changes accompanying the sorption/desorption and resorption/redesorption of CS_2 in initially amorphous PEEK is shown in *Figure 6*. The overall sorption/desorption curves in the virgin and once-sorbed samples are quite similar, although there are several notable differences. The major difference occurs in the rate of resorption compared to the rate of sorption in the original sample. An expanded view of the weight gain as a function of square-root time for the initial sorption and resorption is shown in *Figure 7*. The rate of penetration in the initially amorphous PEEK sample is approximately seven times faster than it is in resorption; this corresponds to a pseudo-diffusion coefficient 50 times greater. During resorption, the sample absorbs 17 wt% compared to 19.4 wt% in the pristine sample, but the resorbed sample exhibits slightly more swelling in the thickness direction: 24% compared to 21% in the virgin material. An expanded view of the first 100 h of desorption (linear time) from both the initial and resorbed samples is shown

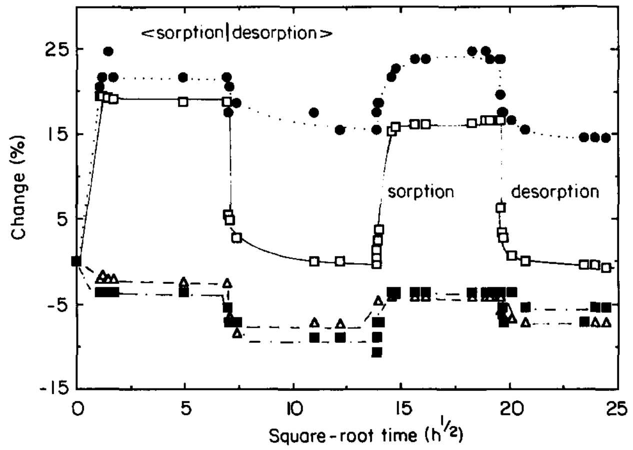

Figure 6 Weight and dimensional changes during sorption (35°C)/desorption (95°C) and resorption (35°C)/redesorption (95°C) of CS_2 from initially amorphous PEEK: □, weight; △, length; ■, width; ●, thickness

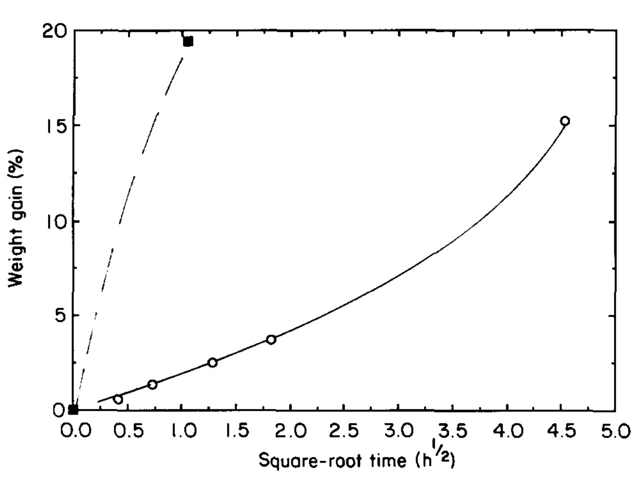

Figure 7 Weight gain during sorption (35°C) and subsequent resorption (35°C) of CS_2 from initially amorphous PEEK: ■, sorption; ○, resorption

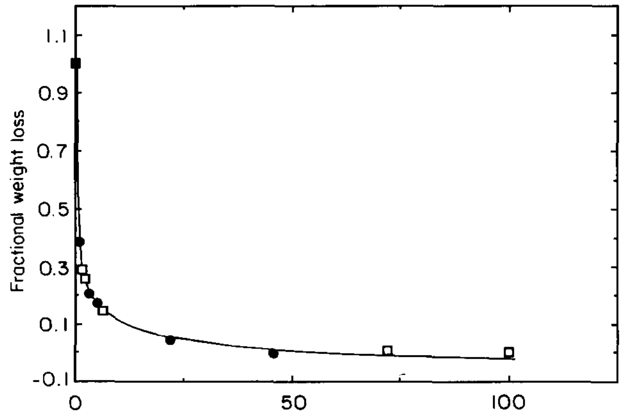

Figure 8 Fractional weight loss of CS_2 from swollen PEEK during the initial and second desorption steps: □, initial desorption; ●, second desorption

in *Figure 8*. The desorption processes are essentially identical. It is important to note that amorphous PEEK undergoes SIC. According to X-ray analysis[13], the crystallinity of an initially amorphous resin following removal of the CS_2 is approximately 34%. Thus, in both cases, desorption occurs from a swollen crystalline sample. When PEEK is crystallized thermally, CS_2 is not readily removed by desorption at 95°C (see *Figure 4*); however, in amorphous material which is crystallized by CS_2, the CS_2 penetrant readily desorbs at 95°C. We have previously shown that the unit cells of the solvent-crystallized samples tend to be tighter and less disorganized than those for thermally crystallized samples[13], and apparently exhibit little or no interaction between crystalline units, i.e. no tie molecules between the crystals.

SUMMARY

The transport of liquids into a semicrystalline thermoplastic material such as PEEK is an extremely complex process. Two liquids, CS_2 and toluene, both exhibit anomalous diffusion and swell the resin. Even though these two liquids are sorbed and swell the resin to essentially the same degree, the rates of sorption are quite different, CS_2 being sorbed orders of magnitude faster. One of the major differences between these two liquids is their molecular geometry. CS_2 is a linear molecule 7.0 Å long with circular diameter 3.3 Å (molar volume 60 cm^3) while toluene is shaped like a cylinder with a bump of thickness 4.0 Å and diameter 8.0 Å (molar volume 106 cm^3). Thus, the geometry of the penetrating molecule may play a major role in the transport into and out of a resin.

Desorption can be resolved into two processes: an initial, rapid desorption and a slow, final desorption. The fast process corresponds to desorption from the plasticized rubbery state in which the rates of diffusion are large. As the diffusant concentration decreases, the T_g of the swollen resin increases until it is equal to the temperature of the desorption chamber. At this time the resin passes from a swollen rubbery material with large diffusion coefficients to a glassy material with much smaller diffusion coefficients. Although the resin undergoes solvent-induced crystallization, the SIC crystals are different to those formed thermally and, in the case of CS_2, have little or no effect upon subsequent desorption. The swelling of the amorphous material is highly anisotropic, the predominant swelling being in the thickness direction; however, in crystalline PEEK the swelling is more nearly isotropic.

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