

Transport of Methylene Chloride in Poly(aryl-Ether-Ether-Ketone) (PEEK) Resin and Composite During Alternate Sorption/Desorption Cycles*

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SYNOPSIS

The transport of methylene chloride into PEEK resin systems following six successive sorption/desorption cycles was investigated. The sorption and desorption processes in neat PEEK with different morphologies and with varying degrees of crystallinity (from 1 to 29%) were compared to chopped-carbon-fiber and carbon-fiber-laminate composites. The amount of methylene chloride sorbed during an 80-min immersion varied from less than 1 wt % in the composites to 37 wt % in the amorphous neat PEEK. During each cycle the solvent was desorbed at 95°C for 338 h. With the exception of the laminate, the sorption/desorption process is essentially independent of cycling. Furthermore, when the desorption processes are viewed in normalized form, i.e., fractional weight loss as a function of time, the desorption appears identical in all samples investigated. Although the maximum amount of solvent retained by the laminate was small, less than 0.1 wt % after the first cycle, it did increase to almost 0.15 wt % after 5 cycles.

INTRODUCTION

Poly(aryl-ether-ether-ketone) (PEEK) is a relatively new thermoplastic resin with great potential for high-performance applications as the matrix material in carbon-based composites; however, it has recently been reported that amorphous PEEK sorbs large quantities of methylene chloride,¹⁻⁶ up to 37 wt % in the amorphous resin.⁴ The solvent advances as a sharp front and the rates of sorption are quite different than those of desorption, i.e., the transport follows Case II kinetics as originally defined by Alfrey⁷ and described by Windle.⁸ Furthermore, the rate of sorption is markedly affected by the morphology (crystallinity) of the resin, which is directly related to its thermal history.

The transport process is quite complex. Both surface effects and bulk-dominated transport have been reported by Grayson and Wolf.⁴ They noted that a small change in morphology, as little as a 3-

4% change in crystallinity, changes the rate of solvent uptake by several orders of magnitude. Stober and Seferis⁵ reported that neat PEEK and single-ply, carbon-fiber prepreg sorbed methylene chloride at the same rate. Furthermore, it has been reported that methylene chloride induces crystallization^{4,5,6} in PEEK. The exact amount of solvent-induced crystallinity is a subject of some discussion. Grayson and Wolf report that the maximum amount of solvent-induced crystallization is 20%, while Stober and Seferis⁵ report induced crystallinities as high as 45%.

The effect of repeated cycles of short-term sorption followed by long-term desorption on the transport of methylene chloride in PEEK is of interest because methylene chloride is known to change the resin morphology and sorption is a strong function of morphology.

Since it is extremely difficult to remove all the methylene chloride from PEEK during desorption, i.e., saturated samples require several thousand hours to remove 99% of the solvent, and the resin is partially crystallized by this solvent, it is quite possible that methylene chloride would accumulate during cyclical transport or could markedly alter the

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transport process. Therefore, we have investigated the transport of this aggressive solvent through six sorption/desorption cycles in neat PEEK with different initial morphologies and in both chopped-fiber composites and carbon fiber laminates.

EXPERIMENTAL

Sample Preparation

Thin Films

Samples of 0.25-mm-thick films of amorphous (Stabar K200) and partially ordered (Stabar XK300) PEEK were obtained from ICI (Wilmington, DE). The amorphous film had a crystalline content on the order of 1–3% and the ordered film had a crystalline content of 27%.

Samples were also obtained from ICI (Wilmington, DE) in the form of injection-molded dogbones made from ICI 450G molding pellets. The samples were in the shape of type 1 specimens as prescribed by ASTM Method 638. During injection molding, the stock temperature was maintained at 360°C and the mold temperature was maintained between 150 and 160°C. Coupons, with dimensions 10 × 3 × 20 mm, were cut from the dogbone-shaped samples; they are referred to as ICI-DB.

Composites

The injection-molded, chopped-fiber composites were prepared by the RTP Co. (Winona, MN) in the form of 2- and 3-mm-thick plaques. The carbon fiber content was 30%. The molding conditions were similar to those for the neat PEEK coupon. The 48-ply (6-mm-thick) laminate was prepared under a pressure of 1.52 MPa (15 atm) at 380°C. The nominal fiber content was 60%.

Solvent Sorption

Sorption was accomplished by immersing the samples in methylene chloride contained in 2.5 × 15 cm culture tubes thermostatted at 35°C. After 80 min, the samples were removed from the culture tubes, blotted dry, and weighed on an analytical balance.

Solvent Desorption

Solvent desorption was accomplished by placing the sample in a sealed culture tube filled with a mixture of a desiccant (Drierite, indicating), and dry, activated charcoal (14 mesh) maintained at 95°C. Solvent weight loss was determined by weighing the samples regularly during the 338 h desorption period.

Physical Measurements

All thick sample edges were machined and all dimensions were measured to the nearest 0.01 mm in three different places. Density measurements were made at selected times before, during, and after sample treatment by the neutral buoyancy method. The crystallinity (%C) was determined directly from the density (ρ) according to the relation of Dawson and Blundell: %C = 1015.4 – 1282.05/ ρ .⁹

RESULTS AND DISCUSSION

Sorption

We have previously shown that CH₂Cl₂ is readily sorbed by PEEK by a classical Case II sorption process, i.e., the solvent advances as a sharp front and desorption is significantly different than sorption. Furthermore, both equilibrium concentration and the rate of solvent diffusion are functions of morphology. The equilibrium concentration in amorphous PEEK is 37 wt % and it decreases approximately 0.5 wt % for each percentage of increase in crystallinity.⁴ The rate of solvent penetration into PEEK is a complex function of morphology in that small changes in crystallinity affect the rate of advance of the sharp diffusion front by as much as two orders of magnitude.⁴

The transport of methylene chloride into the various types of PEEK samples through six successive sorption/desorption cycles is summarized in Figures 1–3.

A feature which was noted previously^{2,4} and occurs in all samples studied is the tremendous difference between solvent sorption and desorption. Sorption is characterized by a linear increase in sample weight with time up to the point of equilibrium solvent content; the sorption rate being a strong function of sample morphology. Desorption is nonlinear, proceeding in a few minutes until about 60% of the solvent has desorbed. The rate of desorption decreases rapidly until it is about $\sim \frac{1}{500}$ th of the initial desorption rate. A small residue of solvent remains in the PEEK resin unless it is heated near the melt temperature. The desorption process is independent of the sample morphology, the number of desorption cycles, and the previous sample history, and can be characterized by two processes, a fast initial desorption in which approximately 60% of the solvent is desorbed in a few minutes, and a slow process. The initial fast desorption

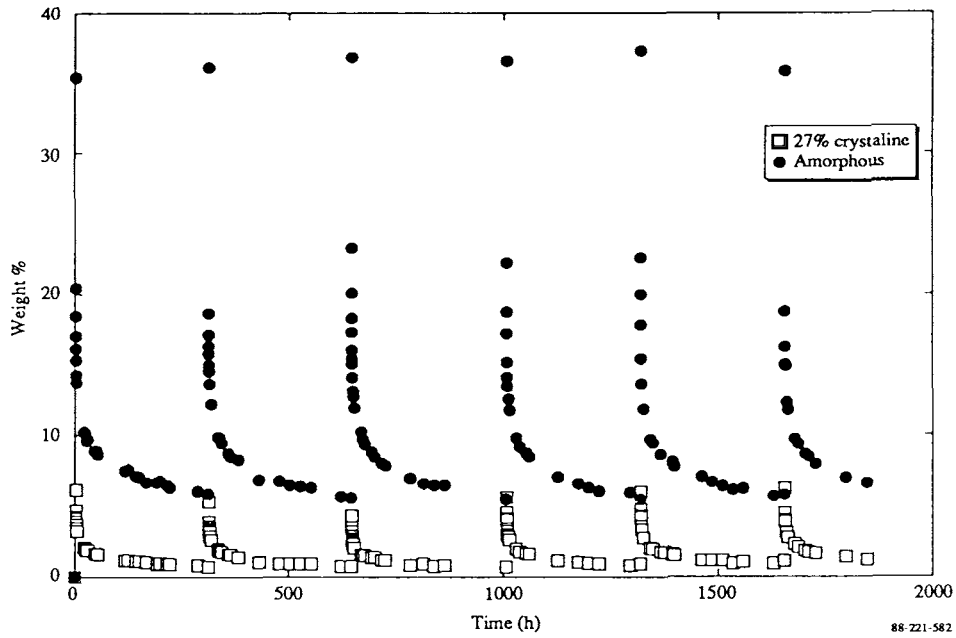


Figure 1 Cyclical sorption/desorption of CH₂Cl₂ in amorphous and 27% crystalline PEEK.

is of the order of 500 times faster than the slow process.

The data for the sorption process are summarized in Table I. The use of percent weight gain to characterize solvent sorption is convenient and useful, especially for samples of the same size; however, for samples of different dimensions, densities, or varying

amounts of resin, percent weight gain can be misleading. A thick sample will exhibit a small percent weight gain even though it sorbs as much solvent as a thin one. A more realistic value which actually represents the transport of the solvent into the resin system is the depth of penetration. Since the solvent penetrates the resin with a sharp front which moves

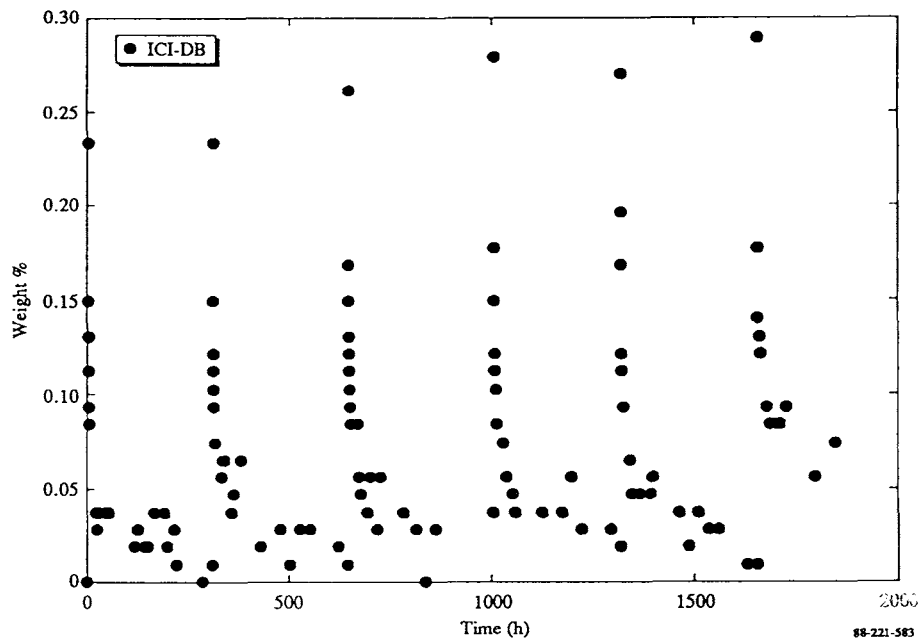


Figure 2 Cyclical sorption/desorption in ICI-DB neat PEEK.

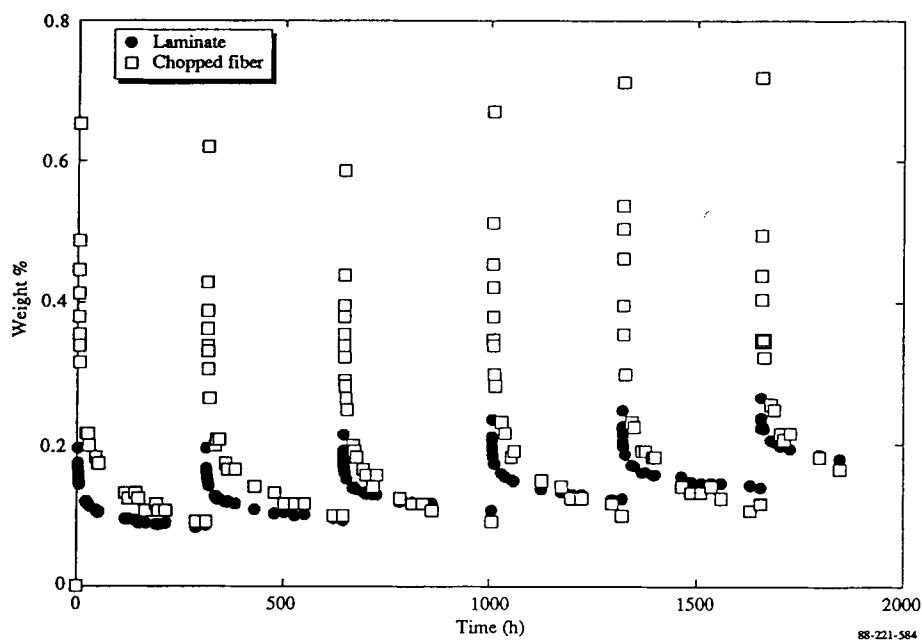


Figure 3 Cyclical sorption/desorption of CH_2Cl_2 in carbon PEEK composites.

linearly with time, it is possible to determine and compare the depth of solvent penetration at the end of a sorption cycle among the different samples. The penetration depth (T_x) can be estimated from the sample geometry, the percent weight gain at the end of a sorption cycle (W_s), and knowledge of the equilibrium methylene chloride content in the samples (W_∞).

The penetration depth is given by

$$T_x = \frac{twl}{A} \frac{W_s}{W_\infty} \quad (1)$$

where dimensions of the sample are l , w , t , and the total surface area is A .

The data summarizing the estimated penetration depths, T_x , in the different samples after the first

(80 min) sorption cycle and following five successive sorption/desorption cycles are given in Table I. The amorphous sample saturates (37 wt %) in less than 10 min while the crystalline film (whose saturation value is 24 wt %) is only one-fourth saturated after 80 min of immersion. Based on the initial slopes of the sorption curve, the rate of sorption in the crystalline Staybar film is 200 times slower than in the amorphous film.

Although the crystallinity of the well-annealed ICI-DB sample is approximately the same as that of the Stabar crystalline film, based on penetration depth, the methylene chloride sorption rate in ICI-DB is approximately one-third that of the Stabar. The sorption rate in both the chopped fiber composite and the laminate are almost equal to that observed in the crystalline film. However, exposed

Table I Summary of Sorption Data

Sample (Dimensions in mm)	% Crystal.	Sorbed 1st Cycle (wt %)	Estimated ^a Depth of Penetration (mm)	Penetration ^b after Five Cycles (mm)
Amorphous Stabar (0.254 × 15.5 × 26)	1	37.0	Saturated	—
Crystalline Stabar (0.254 × 14 × 28.5)	28	6.1	0.032	0.032
ICI-DB (3.2 × 12 × 22)	29	0.23	0.011	0.013
Fiber composite (3 × 10 × 30)	—	0.65	0.040	0.045
Laminate (6.2 × 15 × 45)	—	0.19	0.041	0.054

^a After 80 min immersion.

^b Each cycle consists of 80 min immersion followed by 336 h desorption at 95°C.

fiber ends may contribute to sorption in the composites; this may be particularly significant in the laminate because no precautions were used to seal the ends of the test coupons.

It is important to note that, with the exception of the laminate, methylene chloride does not accumulate during successive sorption cycles. The resin has no memory for previous sorption history. This is rather surprising, especially for the amorphous film, in view of the fact that amorphous PEEK undergoes solvent-induced crystallization. Thus, the solvent-induced ordered regions in PEEK are different from those produced thermally, and solvent-induced crystals have little, if any, effect on the sorption process.

The laminate, on the other hand, is affected by the sorption/desorption history. The amount of methylene chloride retained increases approximately 7% with each successive cycle. After five cycles, the penetration depth has increased to 0.054 mm, a 35% increase in the amount retained. This increase may arise from either a wicking action at the exposed fiber matrix interface or from a markedly reduced rate of desorption as a consequence of the increased diffusion path.

Desorption

The desorption and sorption of methylene chloride in PEEK are quite different processes; desorption is essentially independent of the initial crystallinity or morphology of the resin while sorption is a strong

function of thermal history and morphology. Desorption consists of essentially two processes, an initial rapid desorption and a second, much slower process which depends only upon the temperature of the desorption chamber. The desorption processes in all the samples investigated are quite similar. Normalized plots of the sorption/desorption data are shown in Figures 4–6. In each case, except for the laminate, the ordinate (wt %) of the curves shown in Figures 1–3 was normalized with respect to the averaged maxima observed during each of the six sorption cycles. When viewed in this manner, the similarity of the desorption processes in each of the samples studied is quite apparent.

The desorption curves were deconvoluted into a short-term and a long-term process. The long-term desorption rate for each cycle was determined from a linear regression analysis of the slow desorption portion of each curve. These rates were averaged to give a desorption rate for the five desorption cycles for each material. The rates, together with the standard deviation of this value, are shown in Table II. The desorption rates for all the samples are similar and the average relative rate is $2.45 \pm 0.58 \times 10^{-4} \text{ h}^{-1}$. The values between the highest rate (in the laminate composite) and the rate in the amorphous thin film differ by less than a factor of 2. The values of the long-term desorption rates in the two composites are nearly identical; they are slightly higher than the values observed in the neat resins, but still within a standard deviation of the average value.

The value of the intercept shown in the last col-

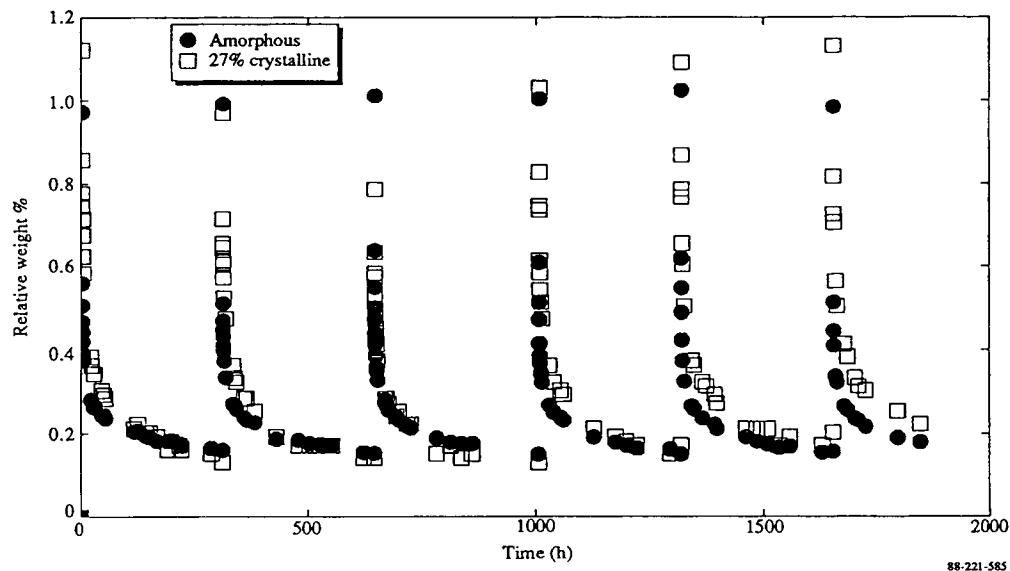


Figure 4 Normalized cyclical sorption/desorption of CH_2Cl_2 in amorphous and 27% crystalline PEEK.

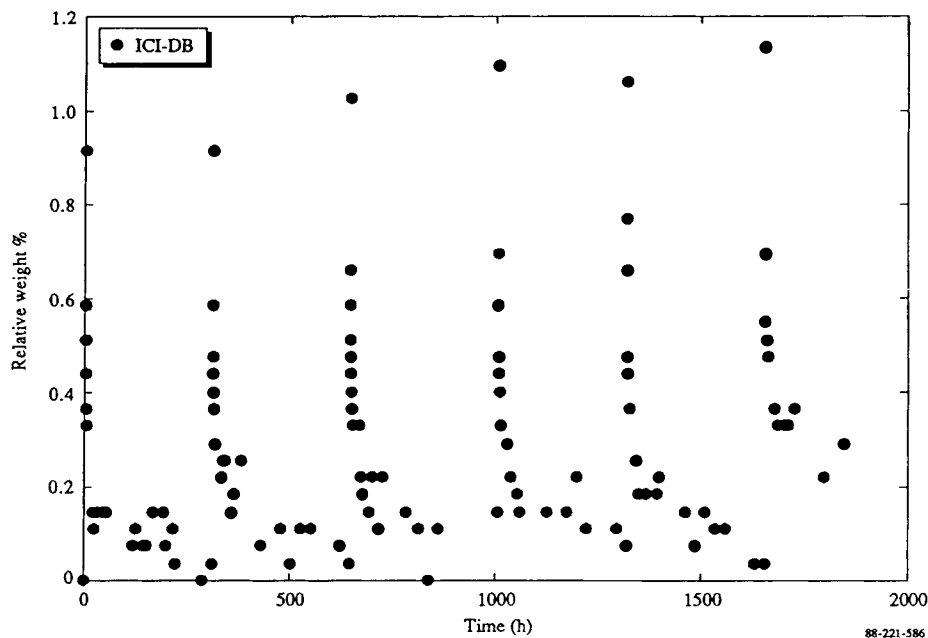


Figure 5 Normalized cyclical sorption/desorption of CH_2Cl_2 in neat ICI-DB PEEK.

umn of Table II represents the fractional amount of methylene chloride desorbed by the slow process. Excluding the laminate data (whose intercept is 0.51), the average value is 0.22 ± 0.4 . This value suggests that in all the samples with different morphologies, inert fillers, and containing different amounts of sorbed methylene chloride, approxi-

mately three-fourths of the solvent is lost by the fast process and one-fourth by the slow process. The laminate is different; approximately one-half of the methylene chloride desorbs by each process, so that in the time intervals employed in these experiments the concentration of the solvent in the resin increases with each successive cycle. The rate of the

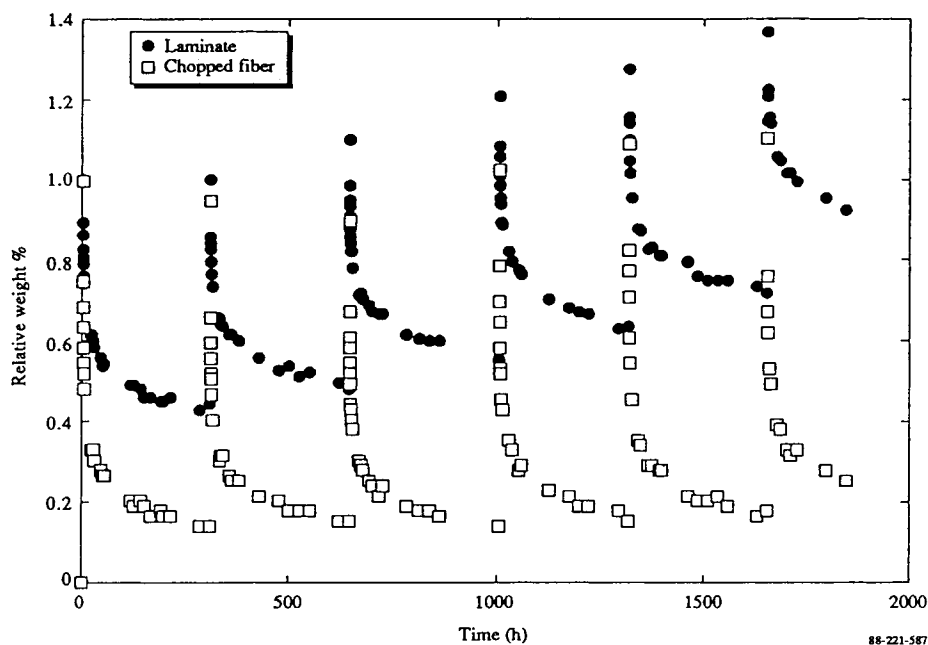


Figure 6 Normalized cyclical sorption/desorption of CH_2Cl_2 in carbon PEEK composites.

Table II Averaged Rates of Desorption Following Cyclical Sorption/Desorption

Sample	Averaged Rate of Desorption (Five Cycles) ($\times 10^{-4} \text{ h}^{-1}$)	First Cycle Intercept
Amorphous (neat)	1.64 ± 0.27	0.23
27% Crystalline (neat)	1.82 ± 0.64	0.25
2 mm ICI-DB (neat)	2.73 ± 1.66	0.16
Chopped-fiber composite	3.03 ± 0.47	0.24
Carbon-fiber laminate	3.06 ± 0.43	0.51

slow desorption process in the laminate appears to be the same as in the other specimens, but less is released by the fast process. We originally proposed that, in addition to temperature, the major factor controlling desorption was the T_g of the swollen resin.^{2,4} It is possible that the T_g of the swollen resin in the laminate is slightly higher than in the other resin systems, thereby reducing the amount rapidly desorbed.

SUMMARY

The cyclical sorption/desorption of methylene chloride in three types of neat PEEK and two carbon-based composites was measured. The solvent moves through the resin with a sharp front at a rate which is strongly dependent upon the morphology and thermal history of the sample. Desorption is a two-step process; in all the samples investigated except the laminate composite, three-fourths of the solvent is removed by a fast process and one-fourth by a slow process with rate of approximately $2.5 \times 10^{-4} \text{ h}^{-1}$. Only half of the solvent is desorbed from the laminate by the fast process.

The major factor controlling the rate of desorption of methylene chloride from PEEK and its composites is the temperature of the desorption chamber. The solvent plasticizes the resin and when the resin is in the rubbery state, i.e., high solvent concentration, the desorption is rapid. As the solvent content in the resin decreases, the T_g increases, approaching the temperature of the desorption chamber. When the T_g is greater than the desorption temperature, the resin is in the glassy state and further desorption of the solvent is extremely slow.

The total amount of methylene chloride remaining in a resin after repeated short-term sorption followed by long-term desorption cycling is small, less than 0.2 wt %, unless the resin is amorphous. Because the sorption process is such a strong function of morphology and thermal history, one might expect that repeated cycling would lead to a buildup of residual methylene chloride after several sorption/desorption cycles, but this is not the case. The desorption process is essentially independent of previous events.

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