Effect of Methylene Chloride Sorption on the Mechanical Properties of Poly(aryl-ether-ether-ketone) (PEEK)*

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Synopsis

The effect of sorbed methylene chloride on the tensile strength and fatigue crack growth (FCG) resistance of PEEK were determined. PEEK sorbs up to 23 wt% methylene chloride; the transport process is essentially Case II, that is, the methylene chloride advances as a sharp front. Sorbed methylene chloride significantly reduces the tensile strength of neat PEEK and the strength reduction is linearly proportional to the amount of solvent sorbed. FCG rates in neat PEEK are increased by the methylene chloride sorption. At saturation, the FCG rates are two orders of magnitude higher than in dry PEEK. Methylene chloride plasticizes the resin, thereby reducing its glass transition temperature (T_g), tensile strength, and FCG resistance.

INTRODUCTION

In the past few years, high-temperature thermoplastic resins have received considerable attention for advanced composite systems. One resin of particular interest is poly(aryl-ether-ether-ketone) [PEEK], manufactured by ICI (England). PEEK is a partially ordered material and the commercially available material is approximately 30% crystalline (by volume).

We recently reported that PEEK sorbed as much as 23 wt% of methylene chloride.[1] The rate of methylene chloride sorption in PEEK is influenced by the surface treatment, thermal processing history, and temperature. Since methylene chloride is an active ingredient used in paint strippers that are widely used on many aerospace systems, it is important to determine the effect of sorbed methylene chloride on the mechanical properties of PEEK.

In this paper, the influences of methylene chloride sorption on the tensile strength and fatigue crack growth (FCG) resistance of PEEK are reported as a function of methylene chloride content. Post fracture surface morphologies of the fatigue-tested specimens were characterized by scanning electron microscopy. The tensile strength and FCG kinetics were correlated to the methylene chloride content and to the fracture surface morphology.

EXPERIMENTAL

Injection-mold, 3-mm thick plaques of neat PEEK were prepared by RTP Company, Winona, Minnesota. These plaques measured 125 × 279 mm and were gated at the center on one surface. The injection nozzle temperature was between 360 and 410°C and the mold temperature was between 160 and 180°C.

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Tensile specimens were machined from molded plaques. The specimen dimensions and test procedures were in accordance with ASTM D638.[2] Fatigue specimens used in this investigation were of the single-edge, compact-tension geometry with a half-height-to-width ratio of 0.6. The stress intensity factor range (ΔK) for this specimen configuration[3] is given by

$$\Delta K = \frac{\Delta P[2 + (a/W)]}{B\sqrt{W}[1(a/W)]^{3/2}}\left[0.886 + 4.64(a/W) - 13.32(a/W)^2 + 14.72(a/W)^3 - 5.6(a/W)^4\right] \quad (1)$$

where ΔP = load range, a = crack length, B = specimen thickness, and W = specimen width. All tensile and fatigue crack growth tests were performed at 293K in a laboratory air environment.

The methylene chloride content in the tensile and compact-tension fatigue specimens was determined gravimetrically and controlled by varying the time of immersion in the 35°C bath; 2-mm thick coupon requires approximately 400 h to reach equilibrium (i.e., 23 wt%). All FCG tests were conducted with constant-amplitude sinusoidal loading at a frequency of 10 Hz and a load ratio of 0.3 with a closed-loop electrohydraulic MTS test machine. The crack advance was monitored with an optical travelling microscope. Fracture-surface morphologies of samples under fatigue loading were characterized by scanning electron microscopy (Amray 1400).

RESULTS AND DISCUSSION

Transport of Methylene Chloride in PEEK

PEEK sorbs a large quantity of methylene chloride, up to 23 wt%, when immersed in the liquid at 35°C;[1] this amount corresponds to approximately one molecule of solvent for each monomeric unit of the polymer chain. The initial weight gain is rapid, corresponding to 1–3 wt% in the first 10–15 min immersion, this is followed by a weight gain which is nearly linear with time to the final saturation value (see Fig. 1, Ref 1). Surface treatment (mechanical abrading) and/or thermal annealing (heating for several hours at temperatures up to 200°C) markedly affect the rate of methylene chloride uptake, but the final equilibrium concentration is not a strong function of thermal or mechanical history and is approximately 23 wt%.

Methylene chloride moves through the resin as a sharp front with a visible boundary separating the dark saturated region from the light-colored virgin PEEK resin. According to energy-dispersive x-ray analysis of the chlorine content in the resin, the boundary region is 20–30 μm wide. Figure 1 shows the relative penetration, as the area of the dark region containing the methylene chloride divided by the total cross-sectional area of a fractured and lightly polished surface, as a function of the weight (%) gained. The line represents the least-squares fit to the experimental data and predicts an equilibrium H_2CCl_2 value (saturation) of 22%, in excellent agreement with the observed value of 23 wt%.

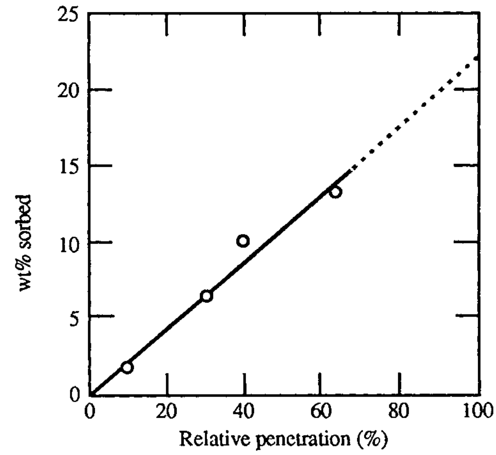

Fig. 1. Weight percent of methylene chloride sorbed as a function of the relative depth of penetration in 2-mm PEEK plaque.

The data suggest that the diffusion process is anomalous Case II[4] and that methylene chloride plasticizes the resin. The partially saturated resin consists of a sandwich-like structure with a layer of virgin resin between two saturated regions.

Tensile Deformation

As shown in Figure 2, the presence of sorbed methylene chloride in neat PEEK significantly degrades its tensile strength; the decrease is linearly proportional to the amount sorbed. The straight line represents the best fit with linear regression analysis. The tensile strength of PEEK saturated with

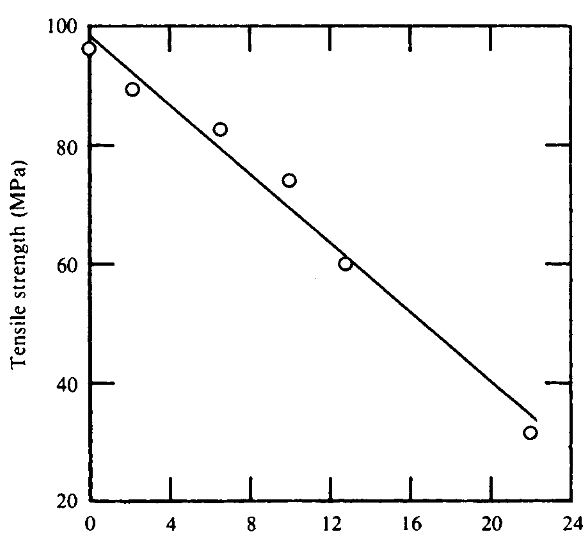

Fig. 2. Effect of sorbed methylene chloride on the tensile strength of PEEK.

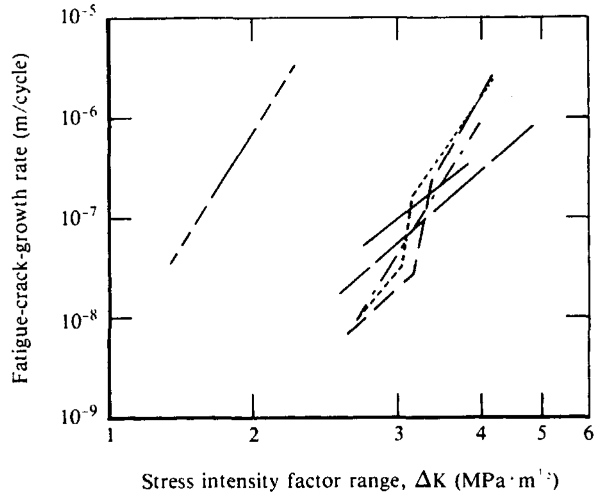

Fig. 3. Effect of sorbed methylene chloride on the fatigue crack growth kinetics in PEEK. Sorbed methylene chloride (%): (——) 0; (—) 2.1; (----) 6.5; (---) 10.0; (------) 13.5; (----) 22.0.

methylene chloride is 32 MPa. Comparison of this value to the neat resin value of 96 MPa reveals that the tensile strength is reduced to one-third its original value. PEEK with and without methylene chloride exhibits uniform deformation in the gauge section of the tensile specimen; thus, although tensile elongation of these specimens cannot be determined, the solvent does not appear to reduce the tensile ductility.

Fatigue Crack Growth

The influence of sorbed methylene chloride on the FCG kinetics of PEEK is shown in Figure 3. PEEK containing 2.1 wt% H_2CCl_2 has a higher FCG rate than the as-received material. Because of the lower modulus and tensile strength, PEEK saturated with 23 wt% methylene chloride exhibits an FCG rate which is more than two orders of magnitude higher than that in dry PEEK. The FCG response for PEEK containing 6.5 to 13.5 wt% methylene chloride are different and are discussed together with the fractographic data.

The fatigue-fracture surface of PEEK containing 10 wt% methylene chloride is shown in Figure 4, in which a clear boundary between the outer saturated region and the central solvent-free region can be seen. This observation directly supports the EDAX measurements described previously,[1] and the sorption measurements summarized in Figure 2; the thickness of the saturated region is directly proportional to the relative amount of solvent. The mechanical properties in the saturated outer region are different from those in the solvent-free central region. Because of the sharp distribution profile of methylene chloride, and the linear relationship between the depth of solvent penetration and the relative saturation amount, the rule of mixtures can be utilized to accurately predict the tensile strength of partially saturated PEEK from the tensile strengths of dry PEEK and fully saturated PEEK.

The fracture-surface morphology in the central, unexposed region of the sample is characterized primarily by transpherulitic fracture. No spherulites

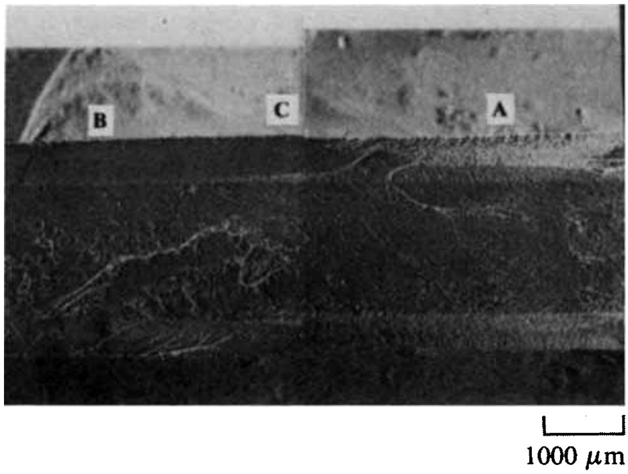

Fig. 4. Fatigue fracture-surface morphology of PEEK containing 10% methylene chloride.

can be seen in the outer saturated region. In the lower ΔK region (region A in Fig. 4), there is considerable evidence of fretting between the two fracture surfaces in the saturated region. The saturated region swells and is under compression, whereas the central unexposed region is under tension. Moreover, as the crack propagates, newly created fracture surfaces are no longer constrained by such a stress distribution; hence, the saturated region of the fracture surfaces bulges. At lower ΔK values, this phenomenon prevents the crack surfaces from closing and induces fretting.

The rough fracture-surface morphology in this region is a result of the fretting. Fretting reduces the effective crack-tip driving force, and results in a lower crack-growth rate in the lower ΔK region of PEEK containing 6.5 to 13.5 wt% methylene chloride. At higher ΔK values, crack opening is significantly large to prevent fretting and FCG assumes a higher rate. Fracture-surface morphology in the outer saturated region at high ΔK values (region B in Fig. 4) is macroscopically smooth and is similar to the fracture-surface morphology of fully saturated PEEK. When observed at higher magnification, there is evidence of craze formation in the smooth region. The transition in FCG rate occurs at ΔK values at which the rough fretting surface begins to disappear (region C in Fig. 4).

SUMMARY

Neat PEEK sorbs up to 23 wt% methylene chloride by anomalous Case II diffusion kinetics, in other words, the solvent moves through the polymer as a sharp front. Methylene chloride reduces the tensile strength by an amount proportional to the wt% sorbed. This suggests that methylene chloride plasticizes the resin, thereby reducing its T_g and tensile strength. Fatigue crack growth rates in PEEK are increased by the methylene chloride sorption. At saturation, the FCG rates are two orders of magnitude higher than the dry PEEK. The anomalous FCG responses in partially saturated PEEK containing 6.5 to 13.5 wt% methylene chloride can be reconciled by the fractographic examination.

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