Environmental Stress Deformation of Poly(ether ether ketone)

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ABSTRACT: The sorption of water in poly(ether ether ketone) (PEEK) from aqueous solutions containing a small (5×10^{-5} mol fraction) of three different surfactants was investigated as a function of external tensile stress. One of the surfactants, a polyoxyethylene alcohol, exhibited a strong stress effect, producing an increase in water solubility of nearly an order of magnitude for stress levels > 40 MPa in amorphous PEEK. The solubility and diffusion coefficient for the sorption of water into PEEK were also investigated. The critical stress (strain) for water sorption, the rate of wetting, and surface deformation morphology were determined. In these aqueous solutions, the primary factor affecting stress-enhanced sorption is a reduction in surface energy and associated surface mobility. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 725–731, 1997

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a semicrystalline thermoplastic polymer which holds great potential for many demanding applications. It is an extremely tough polymer and is considered a high-temperature thermoplastic; the T_g is ~ 145°C, and it has a melting point of 345°C. In addition to its extensive use as a polymer and as the resin in the advanced composite (APC-II supplied by Fiberite), it serves as a model "high temperature" thermoplastic. Although it has been reported to be "insoluble in all common solvents",[1] it is not impervious to these solvents, and it sorbs many organic liquids. The sorption is partially acute for amorphous PEEK, which readily sorbs 20–40 wt % of many liquids including benzene, toluene, carbon disulfide, methylene chloride, and chloroform.[2–9] The sorption of many organic liquids is non-Fickian and appears to follow case II kinetics.[4–9] Furthermore, the appli-

cation of an external stress (or strain) increases both the rate of sorption and the solubility. We call this stress effect SEDS, for stress-enhanced diffusion and solubility.[10] Most glassy, and many semicrystalline thermoplastic polymers, are susceptible to environmental stress crazing and cracking (ESC), although ESC has not been reported to occur in PEEK.

Two general mechanisms have been proposed to account for ESC, a chemical process in which some agent in the environment reacts with the polymer and leads to bond breakage, while the other is a physical process in which some agent in the environment leads to swelling and increased chain mobility accompanied by a decrease in surface energy. In most cases the organic fluid only interacts with the polymer in a physicochemical manner. Moreover, the deleterious effects of ESC are not always immediately obvious; long delays in craze or crack initiation are common under service conditions, particularly when changes in stress level and/or environment take place. Although the solubility of water in PEEK is small, ~ 0.5 wt %,[10] it too exhibits a SEDS effect.[11] A

Table I   Solubility and Diffusion of Water from Surfactant Solutions into Amorphous PEEK

Commercial Name	Chemical Name	Molecular Weight	Molecular Size (cc/gmol)	Solubility Parameter (MPa$^{1/2}$)	Solubility in Water
Scintillating surfactant	ethoxylated octylphenol	646	739	17.1	Soluble up to 10%
Brij 30	polyoxyethylene alcohol	362	381	18	Soluble up to 10%
Sorbitan	sorbitan monolaureate	346	335	18.13	Partially soluble

critical stress (i.e. a value below which SEDS was not observed, of 26 MPa was reported.[11] Additional work on the solubility and effect of water on PEEK is reported, we have expanded this work to include dilute aqueous solutions. Of particular interest is the effect of dilute aqueous solutions containing surfactants on the surface morphology of PEEK.

The phenomena responsible for the stress enhanced sorption of water in PEEK are different from those that have been proposed for the sorption of an organic liquid such as toluene.[11] In the latter case, the enhanced sorption has been attributed to a decrease in the T_g of the polymer until a sufficient quantity of penetrant has been sorbed to change the glassy semicrystalline material to a semicrystalline rubber. The stressed rubber is able to accommodate more penetrant than the unstressed material. In the case of water sorption, the amount of water sorbed is much too small to reduce the T_g of PEEK (T_g = 145°C) to that of the sorption chamber (22°C).

EXPERIMENTAL

Materials

Amorphous PEEK was obtained directly from ICI Americas (Staybar K200) in 8.5 × 11 sheets 0.01 inches (0.25 mm) thick. Test specimens, typically 50 × 5 × 0.25 mm, were cut from the sheets and used directly. The surfactants used in this study, ethoxylated octylphenol (scintillating surfactant, Fisher Scientific Co.), polyoxyethylene alcohol (Brij, Aldrich Chemical Co.), and sorbitan monolaureate (Sorbitan, Aldrich Chemical Co.) were used without further purification. The surfactants, together with important physical properties, are listed in Table I.

Unstressed and Stressed Sorption

Sorption of unstressed films was carried out by immersing the samples in the liquids of interest contained in 2.5 × 15-cm culture tubes placed in thermostatted aluminum blocks. Samples were withdrawn at appropriate intervals, blotted dry, and weighed on an analytical balance. Stressed sorption was carried out by mounting 60 × 5 × 0.25 mm-thick PEEK films in a system of self-aligning grips and pulleys. The entire system was immersed in the fluid of interest. The experiments were actually conducted at constant load; a mass of the appropriate value was placed on a pan at the free end of the pulley system.

Critical Stress Measurements

Critical stress measurements for the polymer in the fluid of interest were carried out with a strain-bending apparatus based on the design of Stoli and Haslett.[12] The test specimens, 50 × 5 × 0.25 mm, were flexed over the surface of the apparatus and conformed to the metal form by clamping at the edges. The apparatus, with film secured, was immersed in the desired aqueous solution. In all cases the concentration of the surfactant in the distilled water was 5×10^{-5} mol fraction. Samples were withdrawn periodically and checked for the appearance of surface cracks. The strain corresponding to the farthest crack advance was noted and the corresponding stress was calculated. The three surfactants were studied at equal mol fractions in order to compare their effect on a molecular basis.

Contact Angle

Contact angle measurements were made at room temperature to determine the wettability of the surfactant/water mixture using a Rhame-Hart A-100 contact angle goniometer. A polymer strip was attached to a glass slide and placed on the observation stage of the goniometer. A single drop (10 μL in volume) of the desired fluid was placed on the polymer surface and the contact angle made by the fluid with the polymer surface was
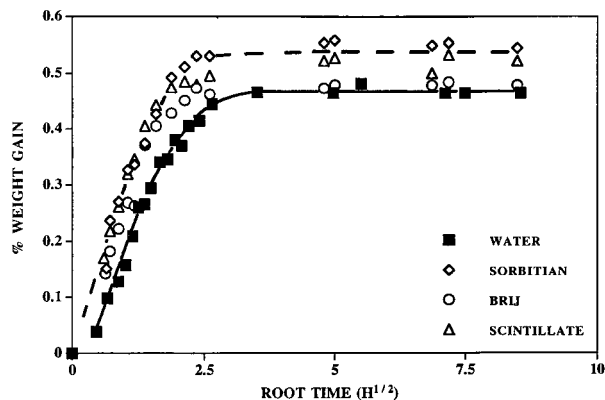
Figure 1 Sorption of water from aqueous surfactant solutions (5×10^{-5} mol fraction) into amorphous PEEK at 24°C.

measured. Wettability of the fluid was calculated by noting the change in contact angle for a 60-s period.[13]

SEM

Morphological analysis of the stressed polymer samples was carried out with a Hitachi S-4500 scanning electron microscope.

RESULTS AND DISCUSSION

The rates of sorption of water at 24°C into thin films of amorphous PEEK immersed in aqueous surfactant solutions, plotted in Fickian form (i.e., weight gain as a function of root-time), are shown in Figure 1. The diffusion coefficient and solubility can be determined from the initial slope of the sorption curve and equilibrium weight gain, respectively. As noted previously,[10] and contrary to that observed for the sorption of organic fluids in PEEK, the solubility increases with temperature. The solubility and diffusion coefficients for the sorption of water into amorphous PEEK films are summarized in Table II. The standard deviation (1σ), based on five to eight values, of the solubility is also listed in Table II.

Diffusion coefficients (D) can be determined from the slope of the linear region of the Fickian plots: D is given by

$$D = \frac{\pi}{16} \, \ell^2 \left(\frac{\text{slope}}{S_o} \right)^2$$

where ℓ is thickness of the film and S_o is the equilibrium weight gain (solubility). In all cases the linear correlation coefficient (r) was > 0.96 and indicates a good fit to a linear equation. The error in the diffusion coefficient is estimated to be $\sim 10\%$. Assuming a simple Arrhenius-type equation based on just two temperatures, the temperature coefficient for diffusion of pure water is ~ 42 kJ/ mol, in excellent agreement with the previously reported value of 42.1 kJ/mol.[10]

The solubility in the presence of the surfactant is $\sim 10\%$ greater than in pure water. At 24°C the diffusion coefficient is approximately twice as fast in the surfactant solutions as in pure water, but at 60°C the average diffusion coefficients in the presence of surfactant are only 25–30% greater than those in pure water. The temperature coefficients for diffusion, determined from the Arrhenius equation, are listed in Table II. The estimated error in these values is $\sim 25\%$. Nevertheless, the values observed for the surfactant solutions are $\sim 50\%$ lower than those observed in pure water.

In a manner similar to that reported previously, we examined the effect of external stress on the sorption of water from the surfactant solutions. These results are summarized in Figures 2–4 for the sorption of water from the Brij, Sorbitan, and Scintillate solutions (5×10^{-5} mol fraction) at 24°C, respectively. The applied stress varied from 0 to 50 MPa.

Similar plots were obtained for the sorption of water into amorphous, 13% and 29% crystalline PEEK. The equilibrium weight gain, that is, solubility, at 24° and 60°C as a function of applied load (stress) is shown in Figure 5(a,b). The solubilities in the 13% and 29% crystalline PEEK are essentially identical, equal to 0.43 wt % at 24° and ~ 0.47 wt % at 60°C. If crystalline PEEK was a two-phase system, with an independent amorphous crystal phase, one would expect the solubility of the crystalline material (S_c) to be the sum of the contributions from each phase, that is,

$$S_c = \phi_a S_a + \phi_x S_x$$

where ϕ represents the volume fraction of the amorphous and crystalline phase (x) and S the solubility in the pure phase. The solubility in the crystal is usually so much smaller than in an amorphous region that the contribution from the crystalline region is assumed to be zero; therefore,

$$S_c = \phi_a S_a$$

Table II Solubility and Diffusion of Water from Surfactant Solutions into Amorphous PEEK

Solution	Concentration (mol fraction)	Temperature (°C)	Solubility (wt %)	Heat of Solution (kJ/mol)	Diffusion Coefficient ($\times 10^{-12}$ m²/s)	Activation Energy (kJ/mol)
Distilled water	—	24	0.47 ± 0.01		0.59	
Distilled water	—	60	0.54 ± 0.02	3.2 ± 1	3.7	42 ± 2
Sorbitan/H_2O	5.2×10^{-5}	24	0.55 ± 0.01		1.3	
Sorbitan/H_2O	5.2×10^{-5}	60	0.64 ± 0.02	3.4 ± 1	3.8	24 ± 6
Brij 30/H_2O	5.2×10^{-5}	24	0.47 ± 0.01		1.2	
Brij 30/H_2O	5.2×10^{-5}	60	0.58 ± 0.02	4.8 ± 1	5.0	32 ± 8
Scintillate/H_2O	5.2×10^{-5}	24	0.51 ± 0.02		1.4	
Scintillate/H_2O	5.2×10^{-5}	60	0.52 ± 0.03	10.5 ± 0.5	4.9	28 ± 7

Thus, the solubility in amorphous, 13%, and 29% would be in the ratio of 1.0 to 0.87 to 0.71, respectively. Clearly this is not the case, and if crystallinity were the prime factor affecting solubility, the solubility values would be different. Solubility increases with applied stress, but the overall increase is much smaller in the crystalline than in the amorphous material.

The SEDS sorption in the Brij solution is quite different from that observed in the other solutions; it exhibits a large and pronounced stress effect. The other solutions, including water, show a small increase in solubility for stresses $> 25-30$ MPa; however, in the Brij solution, the solubility increases almost an order of magnitude for an applied stress of 50 MPa. It is important to note that the tensile strength of PEEK has been reported

to vary from ~ 60 to 100 MPa; the manufacturer[14] has reported an ultimate strength of 120 MPa. Measurements in our laboratory indicate that the tensile strength of amorphous PEEK (engineering value) is ~ 65 MPa. Thus, the maximum stress used in these experiments, 50 MPa, is significantly below the yield strength of the polymer.

One would expect that the primary effect of a surfactant is to lower the surface energy at the polymer–liquid interface and accelerate the wetting of the polymer surface by the solution. The concept of wetting and diffusion are related; wetting, or more properly the rate of spreading on a surface, is indicative of the time for the liquid to reach equilibrium on the polymer surface. Therefore, surface tension and rate of spreading were
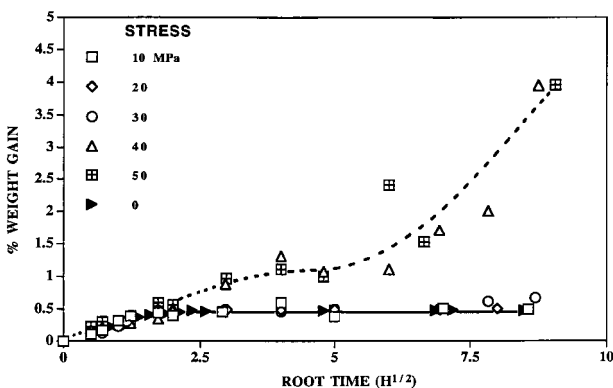
Figure 2 Weight gain curve (Fickian plot) for the sorption of water from Brij solution into amorphous PEEK at 24°C at various applied stress levels.
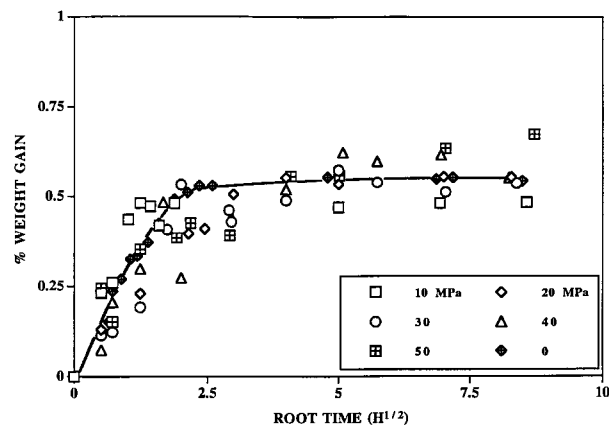
Figure 3 Weight gain curve (Fickian plot) for the sorption of water from soribitan solution into amorphous PEEK at 24°C at various applied stress levels.
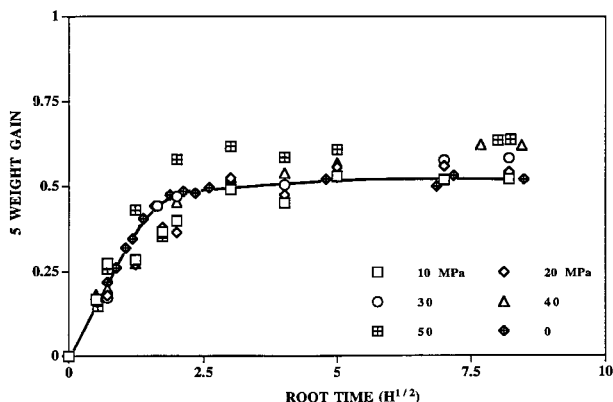
Figure 4 Weight gain curve (Fickian plot) for the sorption of water from scintillate solution into amorphous PEEK at 24°C at various applied stress levels.

measured by the sessile drop method. The results are reported in Table III, where the contact angle after 5 and 60s are listed together with the rate of change. The rate of change measures the rate of spreading across the surface and is related to the strength of the interaction between the solution and the polymer. Although the Sorbitan is considered an aqueous surfactant, the rate of spreading, hence the attractive forces, is essentially the same as that of pure water. Brij, on the other hand, exhibits rapid spreading and large interaction potential.

The stress (or strain)–time relationship was investigated by using the bending form method described by Stokki and Hoslet.[12] The time required for a given stress to produce visible surface cracks, or surface yielding, was measured as a function of strain. The strain (ε) was related to the stress (σ) by the simple form of Young's modulus (E)

$$\sigma = E \cdot \varepsilon$$

The numerical value calculated for stress is in direct relation to the value chosen for Young's modulus, we used a value of 2.0 GPa. The critical value (ε_c, σ_c) for the formation of surface yielding was obtained as the lowest value of strain (or stress) to produce surface deformation after several hundred hours' immersion. A plot of the stress required to produce surface cracking (at 60°C in a 5×10^{-5} mol fraction solution) as a function of time is shown in Figure 6. The critical stress can be estimated by a linear extrapolation to the stress axis: the estimated critical values are: 13, 23, 23, and 19 MPa for Brij, Scintillate,

Sorbitan, and pure water, respectively. These values are only approximate values but indicate that the critical stress for the Brij solution is ~ 50% lower than that of pure water, and 50–75% lower than either the Scintillate or Sorbiton solutions. Although the critical stress in pure water is less than in either the Scintillate or Sorbitan solutions, the time required for surface deformation is much greater, which indicates the importance of surface energetics, that is, rate of wetting.

The Brij solution had the most pronounced effect on the polymer. The sample yielded in 36 h at a stress level of 40 MPa; the yielding was uniform and occurred at both ends of the sample and was accompanied by severe cracking and cavitations along the entire length of the sample. A photomicrograph exhibiting the surface cracks on amorphous PEEK following immersion (64 h) in Brij solution (5×10^{-5} mol fraction) at 24°C while stressed to 50 MPa is shown in Figure 7. The average distance between surface cracks in this severely degraded surface is approximately 6 μm. The cavitation is clearly visible at higher magnification (Fig. 8).
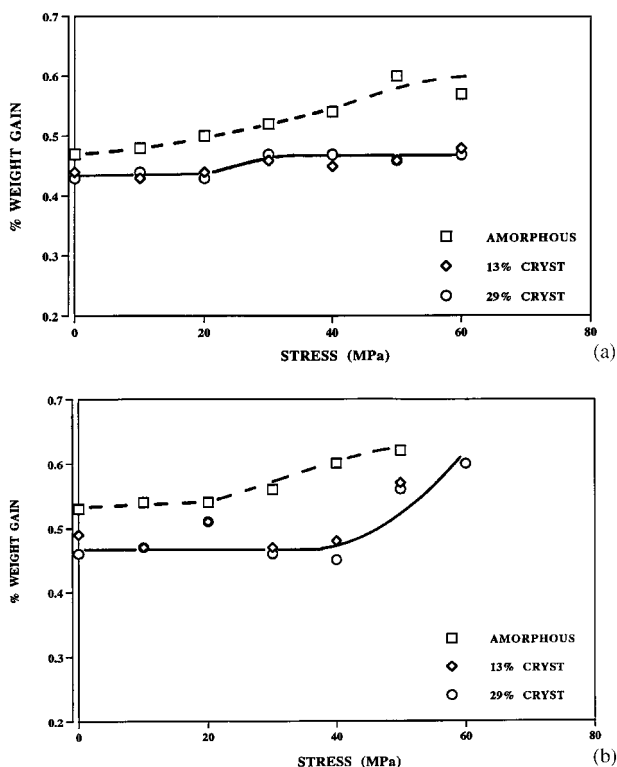

Figure 5 (a) Solubility of water in PEEK at 24°C as a function of applied stress and morphology. (b) Solubility of water in PEEK at 60°C as a function of applied stress and morphology.

Table III   Contact Angle Measurements on Aqueous Surfactant (5×10^{-5} mol fraction) Solutions at 24°C

Solution	Contact Angle (5s)	Contact Angle (60s)	Rate of Wetting[a] (deg/s)
Distilled Water	55°	51°	0.073
Brij	21°	2°	0.345
Scintillate	25°	14°	0.20
Sorbitan	45°	42°	0.055

[a] Rate of wetting = Δ angle/Δ time.

The enhanced sorption of water from the Brij solutions for stresses > 40 MPa (see Fig. 3) is accompanied by severe cavitation and surface deformation noted in Figures 7 and 8. A sample of PEEK immersed in the Sorbitan mixture also begins to show cracking when stressed at 40 MPa for > 50 h. However, only a few cracks were observed and they are more randomly distributed on the polymer surface. The third surfactant solution, Scintillate, exhibited a most unusual effect: samples stressed for > 70 h at 40 MPa yielded to an extension of > 100% without any evidence of cracking. An obvious difference in Scintillate and either Sorbitan and Brij is molecular size; the scintillate molecule has a molar volume of 739 cm³/mol compared to 381 and 335 cm³/mol for Brij and Sorbitan, respectively. The molecular size was estimated with the aid of a commercial molecular simulation package (QUANTA) to be 451, 270, and 219 cm³/mol for the Scintillate, Brij, and Sorbitan, respectively. Scintillate is approximately twice as large as either of the other surfactants. However, Brij and Sorbitan are approximately the same size, and Brij is much more effective in promoting yielding than Sorbitan.
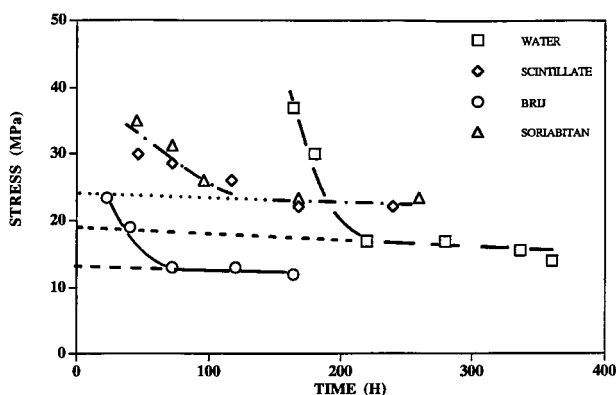

Figure 6   Time-to-fail in aqueous solutions as a function of stress at 24°C.

CONCLUSIONS

Extensive reviews have been written on ESC, for example see ref. 15, but it is generally assumed that the closer the solubility parameter of the agent and the polymer, the more likely ESC will occur. Of course other factors, such as molecular size, are important, but solubility parameters are usually considered the single most important factor. We do not observe the classical cavitation and stress whitening which is characteristic of environmental stress crazing; we observe deformation zones containing homogeneously stretched material. The exact cause of this deformation is not known; however, plastification effects alone are not sufficient to explain the observed effects. In the experiment reported herein, PEEK is always in the glassy state since the T_g is 145°C. We have shown previously that the sorption of sufficient quantities of organic fluids into PEEK lowers the
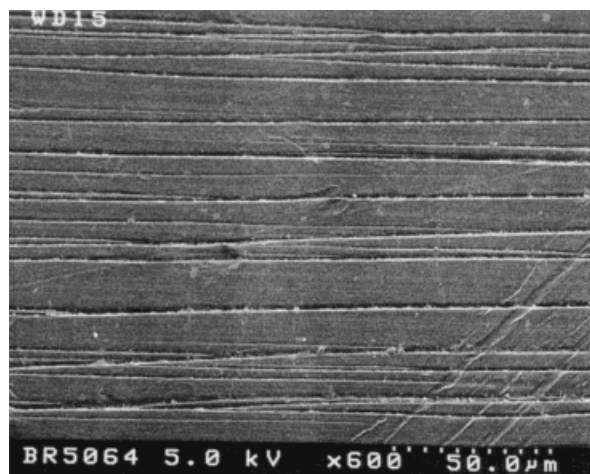
Figure 7   Photomicrograph of PEEK stressed to 50 MPa immersed in an aqueous solution of Brij for 64 h: low magnification (600×) showing high concentrations of surface cracks.
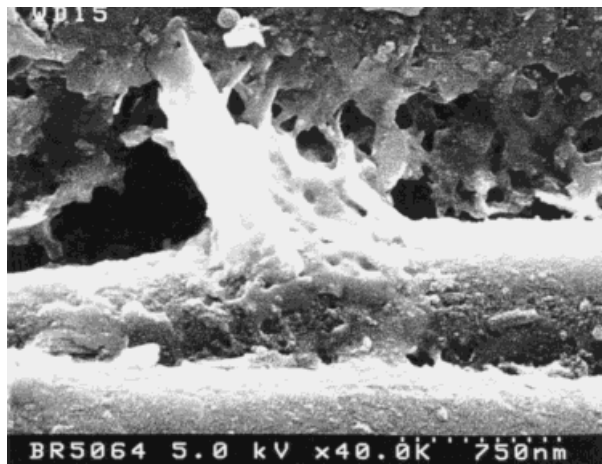
Figure 8 Photomicrograph of PEEK stressed to 50 MPa immersed in an aqueous solution of Brij for 64 h: high magnification (4000×) showing cavitation at the surface crack.

T_g of the swollen system to that of the sorption chamber. For example, the sorption of 16 wt % toluene into PEEK is sufficient to reduce the T_g of the swollen PEEK/toluene to 22°C.[9] However, the quantity of water sorbed by the amorphous PEEK is not sufficient to lower the T_g of the polymer to that of the sorption bath. According to Fox[16] the relationship between the T_{gR} of the swollen polymer and the amount of penetrant sorbed is given by

$$\frac{1}{T_{gR}} = \frac{\omega_P}{T_{gP}} + \frac{\omega_S}{T_{gS}}$$

where ω_P and ω_S are the weight fractions of the polymer and penetrant in the swollen polymer, and T_{gP} and T_{gS} are the T_g of the pure polymer and penetrant, respectively. Even for the maximum sorption observed in this study, 4 wt % (Brij at stress > 40 MPa), the T_g of the swollen resin would be only reduced to 387 K (114°C) since the T_g of the resin and water are 418 and 139 K, respectively. For most of the samples investigated, the decrease in T_g would be less since the maximum amount of water sorbed is < 1 wt %. Thus, we conclude that the enhanced sorption and sur-

face deformation are due to surface energy effects rather than a lowering of T_g. This effect is quite different from that observed in the sorption of organic fluids, such as toluene, carbon disulfide, or methylene chloride, in PEEK, which exhibits pronounced swelling accompanied by a transition to the rubbery region. Although pure water does exhibit a small SEDS effect, the phenomenon is much more pronounced in the presence of the surfactant, Brij, which shows rapid spreading across the polymer surface and, when highly stressed, yielding accompanied by cavitation.

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