Water Sorption Kinetics in
Poly(aryl Ether Ether Ketone)

G. MENSITIERI, A. APICELLA, J. M. KENNY and L. NICOLAIS,
Department of Materials and Production Engineering, University of Naples, Piazzale Tecchio 80125, Naples, Italy

Synopsis

The kinetics of diffusion of water from different activity vapors and liquid phase have been investigated in glassy amorphous poly(aryl ether ether ketone) (PEEK) films at the temperature of 60°C and in glassy semicrystalline PEEK sheets at different temperatures, respectively. In the case of the amorphous PEEK films (250 μm thick) the data at low activity levels were interpreted by means of a purely Fickian mechanism. At higher activity levels the material has shown the presence of a relaxation process; in this case the data have been interpreted using a model proposed by Berens and Hopfenberg. Equilibrium sorption isotherm is also reported. Liquid water sorption in semicrystalline (30%) PEEK sheets (2 mm thick) has been determined to follow the classical Fickian mechanism. The water uptake values obtained for both amorphous and semicrystalline PEEK, confirm the good moisture and liquid water resistance of this kind of high performance thermoplastic polymer.

INTRODUCTION

Fiber-reinforced polymeric composites are currently used in structural applications where high strength combined with light weight is of critical importance. In such applications the composites are expected to be exposed to mechanical fatigue as well as to extreme environmental conditions such as freezing and thawing at high humidity over a wide range of temperatures. The matrices actually used are generally restricted to the class of epoxy resins. Moreover, the demand of a drastic increase in strength through an increase of strain to failure, which follows from the interest to improve the impact resistance and damage tolerance of these structural composite materials, promoted the investigation of alternative matrices. However, although a number of epoxy resin systems with modified impact toughness have come into the market, the response of such systems in actual conditions of use is often unsatisfactory. In this context, temperature stable thermoplastics have been considered for use with high-performance fibers. These new thermoplastic based composites show adequate strength and stiffness at elevated temperatures coupled with a good chemical resistance.

In particular, poly(aryl ether ether ketone) (PEEK) is a tough aromatic polymer with attractive high performances. It is a semicrystalline polymer with melting point of about 335°C and a glass transition of about 145°C. The morphology and related properties of PEEK are well described in the work of Blundell and Osborn[1] and in a recent paper of Carfagna et al.[2]

Although the properties in the fiber direction of these reinforced materials are mainly determined by the fiber properties, the application limits are in

many cases governed by the type and characteristics of the matrix. In particular, the resistance to different environmental conditions (mainly hygrothermal changes) is one of the most important matrix properties. Generally, also at ambient conditions, low molecular weight substances may easily migrate into the polymers by a solution–diffusion mechanism. Addition of moisture to an amorphous polymer usually reduces its glass transition temperature. In particular, the high moisture sensitivity of the epoxy matrices is due to the strong interactions between the water molecules and some groups present in the polymer structure. This process results in a depression of the glass transition and a loss of mechanical properties of the epoxy composites.[3]

Conversely, in a preliminary investigation[4] PEEK proved to be highly resistant to water. Characterization of sorption and desorption behavior of PEEK in fluids was made for films of different crystallinity,[4] and a small value of water solubility has been reported; but the diffusion behavior has not been described.

A more detailed analysis of the solubility and diffusion of water in semicyrystalline (30%) PEEK has been recently reported.[5] It has been found that the solubility of water increases from 0.44 to 0.55 wt % ranging from a temperature of 35 to 95°C. The diffusion has been determined to follow the classical Fickian mechanism, and no change in the matrix morphology has been detected during the sorption and resorption cycles.

Glassy polymers generally exhibit a complex transport behavior. Both concentration-gradient-controlled diffusion and relaxation-controlled swelling contribute to the rate and extent of penetrant sorption. A wide variety of effects are exhibited depending on the polymer–penetrant system, on the temperature, and on the penetrant activity and concentration. Varying the temperature and the penetrant activity in a given system, it is possible to investigate the full range of behavior, from ideal Fickian diffusion to limiting Case II, as suggested by Hopfenberg and Frisch.[6]

A criterion for predicting whether the transport is diffusion- or relaxation-controlled has been proposed by Vrentras et al.[7] in the form of a dimensionless number called "diffusive Deborah number." This criterion is based on the relative importance of the characteristic diffusion time (l^2/D) compared to a mean relaxation time (τ). An exhaustive study showing examples of these effects has been performed for VCM monomer, acetone, and methanol diffusion in PVC and n-hexane diffusion in polystyrene.[8,9]

In the present work water vapor sorption at different activities in neat glassy amorphous PEEK films (250 μm thick) is investigated at a temperature of 60°C. Diffusion data and equilibrium sorption isotherm are evaluated. Moreover, liquid water sorption measurements in semicrystalline (30%) PEEK thicker sheets (2 mm) have been performed at different temperatures, evaluating the activation energy related to the diffusion mechanism.

EXPERIMENTAL

Materials

Amorphous PEEK (ICI) films of thickness of 250 μm and semicrystalline (30%) sheets of thickness of 2.0 mm were utilized in the vapor and liquid
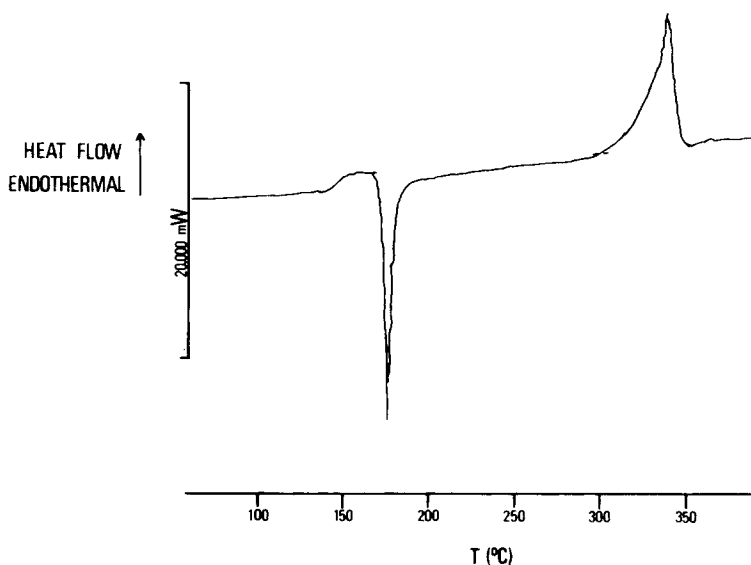
Fig. 1. DSC heating scan at 10 K/min rate for amorphous PEEK.

sorption tests, respectively. The samples were analyzed to verify the degree of crystallinity using a differential scanning calorimeter (DSC, Mettler TA 3000 System), a Fourier transforms infrared spectrometer (FTIR, Nicolet 5DX), and a density gradient column (DGT), consisting of a $Ca(NO_3)_2$ solution, having a sensitivity of 2×10^{-2} $g/(cm^3 m)$.

DSC scans were performed at a heating rate of 10 K/min, and values of 30% crystallinity for the semicrystalline samples and less then 1% for the "amorphous" films were determined.[10] Figure 1 shows a thermogram relative to an "amorphous" sample: The sum of low temperature "cold crystallization" peak area and melting peak area is practically zero.

The FTIR absorbance spectrum relative to the amorphous samples showed the absence of the absorbance peak in correspondence to a wavelength of 970 cm^{-1} characteristic of the crystalline structure.

The density measurements conducted on the amorphous samples showed a density value of 1.266 g/cm^3 that is close to the value associated with a totally amorphous sample.[1]

Apparatus and Procedures

Water Vapor Sorption

For these experiments an electro-balance (C. I. Electronics Ltd. Co., Cahn type microbalance) mounted in a glass-vacuum chamber was used. The balance chamber is positioned in a box equipped with a hot air circulating system for the temperature control. The balance is connected to an external container of distilled and degassed liquid water, kept at controlled temperatures, capable of supplying water vapor at variable pressures. In this way it is possible to obtain different constant relative humidities in the balance chamber and in a large volume flask connected to the system. The apparatus can readily be

evacuated (10^{-5} torr) by means of an "Edwards" high-vacuum diffusion pump.

All the experiments were made at a temperature of 60°C. The chamber was first evacuated until a constant sample weight was achieved; then water vapor was admitted at a selected pressure. The "lung" flask avoids pressure instability in the first moments of the experiment.

The samples were submitted to alternate sorption–desorption cycles at increasing water vapor relative pressures.

Liquid Water Sorption

The samples were immersed in liquid distilled water at controlled temperatures. At regular intervals, the samples were removed from the water, blotted, placed in a weighing bottle, weighed, and finally replaced in the constant temperature water bath.

RESULTS AND DISCUSSION

Water Vapor Sorption in Amorphous PEEK

Data of water gain in the form of percent water uptake relative to the dry polymer weight vs $\sqrt{t}/l$ (where l is the sample thickness) for different water activities (a) at a temperature of 60°C are reported in Figures 2(a, b, c, d). In the same figures the curves representing the purely Fickian diffusion model are shown. The Fickian diffusion coefficients were evaluated by means of the following formula:

$$D = (\pi/16)\left(l/\sqrt{t^*}\right)^2 \tag{1}$$

where l is the sample thickness and t^* is the time at which the straight line fitting the first points crosses the horizontal line relative to the equilibrium uptake. The values of D are reported in the caption of Figure 2. The diffusion coefficients evaluated in this way were substituted into the solution for sorption in a plane sheet as given by Crank[11]:

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} \left\{ \frac{8}{(2n+1)^2\pi^2} \cdot \exp\left[-\frac{D(2n+1)^2\pi^2 t}{l^2} \right] \right\} \tag{2}$$

Since the sample thickness was very small compared to the surface area, no edge correction procedure was adopted in the evaluation of the diffusion coefficients.

The model given by the application of Eq. (2) provides a very good data fitting in case of low and medium water activities. The sorption curve relative to $a = 0.35$ and the successive desorption data are reported in Figure 3. The data obtained in the two experiments overlap very well, indicating the absence of a dependence of D on the water concentration inside the polymer. The purely Fickian diffusion model fails to provide a totally satisfactory representation of the data points in the case of higher water activities. The shape of the final part of the sorption curve suggests that a relaxation process is

superimposed to the Fickian sorption. This swelling–relaxation process can either overlap or follow the Fickian behavior depending on the molecular mobility.

A criterion to discriminate if the process is diffusion- or relaxation-controlled was proposed[7] in the form of a dimensionless "Deborah" number:

$$(DEB)_d = \tau/\theta \tag{3}$$

where τ is a mean relaxation time and θ represents a characteristic time of the diffusion process equal to the ratio l^2/D. If $(DEB)_d \gg 1$, the characteristic time of the relaxation process is some order of magnitude greater than the time associated with the diffusion mechanism. This implies a separation of the two processes: I.e., first an apparent equilibrium is achieved by means of a purely Fickian mechanism; subsequently, a slow relaxation process leads to a true thermodynamic equilibrium. Conversely, if $(DEB)_d \ll 1$, the mass transport is diffusion-controlled, and the two mechanisms act contemporarily.

It can be argued that if the experimental time is short enough, the sorption follows a Fickian mechanism independently of the value of $(DEB)_d$ even if the
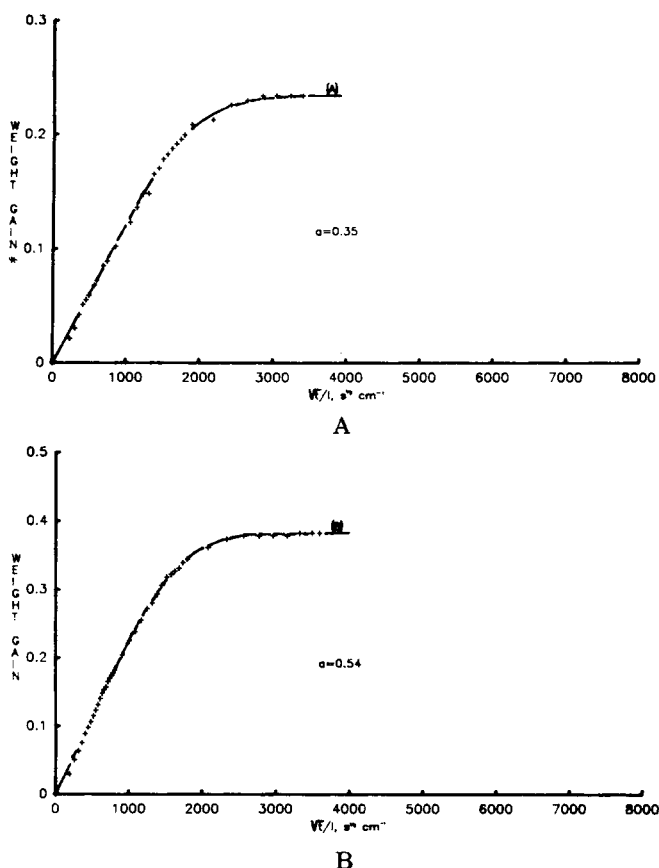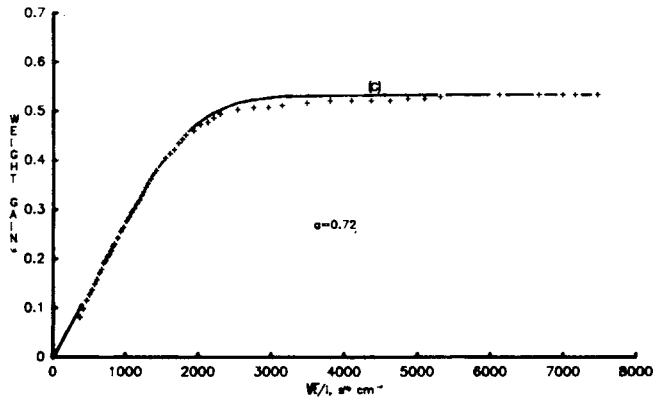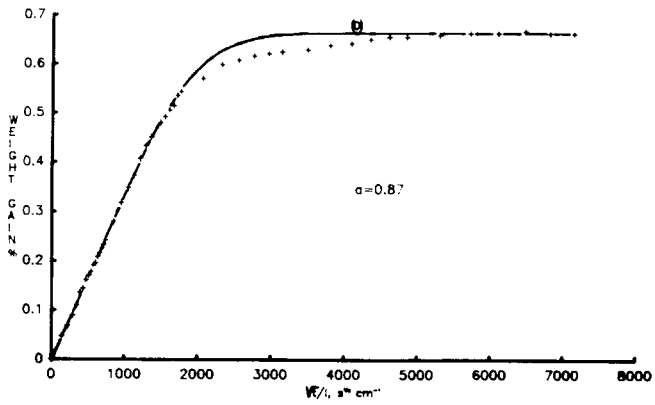

Fig. 2. Water vapor sorption kinetics at different activities in a 250 μm thick amorphous PEEK film. The full lines represent the Fickian eq. (2) using the diffusion coefficients evaluated with eq. (1): (A) $a = 0.35$, $D = 5.3 \times 10^{-8}$ cm^2/s; (B) $a = 0.54$, $D = 6.7 \times 10^{-8}$ cm^2/s; (C) $a = 0.72$, $D = 5.2 \times 10^{-8}$ cm^2/s; (D) $a = 0.87$, $D = 5.0 \times 10^{-8}$ cm^2/s.

C

D

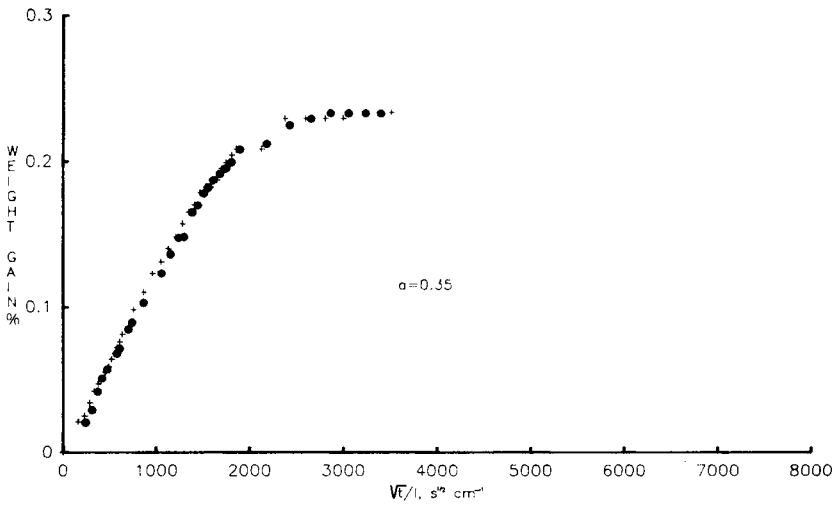Fig. 2.   (*Continued from the previous page.*)

Fig. 3.   Percent weight gain for water vapor sorption (●) and desorption (+) in a 250 μm thick amorphous PEEK film.

two situations are substantially different. In the first case [(DEB)$_d \gg 1$], the process is called "elastic diffusion," and in the second case [(DEB)$_d \ll 1$], "viscous diffusion." Finally when (DEB)$_d$ is about 1, the two mechanisms have the same characteristic times. This is a case of anomalous diffusion also called "viscoelastic diffusion." The geometric factor (l) is very effective in determining the sample behavior as referred for benzene sorption in PET sheets[12] and moisture sorption in epoxy resins[13] below their glass transition.

For the sake of interpretation of the sorption behavior at higher activities, the model proposed by Berens and Hopfenberg[9] in their analysis of VCM monomer and n-hexane sorption, respectively, in PVC and polystyrene glassy powders has been used. This model considers the linear superposition of a Fickian diffusion contribution and a first-order relaxation term and attributes to each mechanism a fixed fraction of the total sorbed solvent equilibrium amount.

At time t the amount of solvent sorbed is given by

$$M(t) = M_f(t) + M_r(t) \tag{4}$$

where $M_f(t)$ and $M_r(t)$ are, respectively, the Fickian and relaxation contributions. The first contribution is

$$M_f(t) = M_{\infty f} \left[1 - \sum_{n=0}^{\infty} \left(\frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left(-\frac{D \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{l^2} \right) \right) \right] \tag{5}$$

The second one, due to relaxation, is

$$M_r(t) = M_{\infty r} \cdot [1 - \exp(-kt)] \tag{6}$$

where k is the relaxation rate constant. This term considers a single characteristic relaxation time. $M_{\infty f}$ and $M_{\infty r}$ represent the equilibrium amounts of water uptake due to the Fickian diffusion and relaxation, respectively.

Substitution of eqs. (5) and (6) into eq. (4) gives the following model:

$$M(t)/M_\infty = \phi_f \cdot \left\{ 1 - \sum_{n=0}^{\infty} \left[\frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left(-\frac{D \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{l^2} \right) \right] \right\}$$
$$+ (1 - \phi_f) \cdot [1 - \exp(-kt)] \tag{7}$$

where $\phi_f = M_{\infty f}/M_\infty$ and $M_\infty = M_{\infty f} + M_{\infty r}$.

This model provides a good interpretation of the experimental results obtained at the highest activities as shown in Figures 4(a, b). In these figures the best-fitting values of the parameters appearing in the model (D, ϕ_f, and k) are also reported. In these cases, the calculated value of (DEB)$_d$ is about 1, and therefore the small thickness of the sample allows us to distinguish the two mechanisms.

It must be emphasized that at low activity levels this double mechanism was not observed. In such conditions the solvent-induced relaxations are
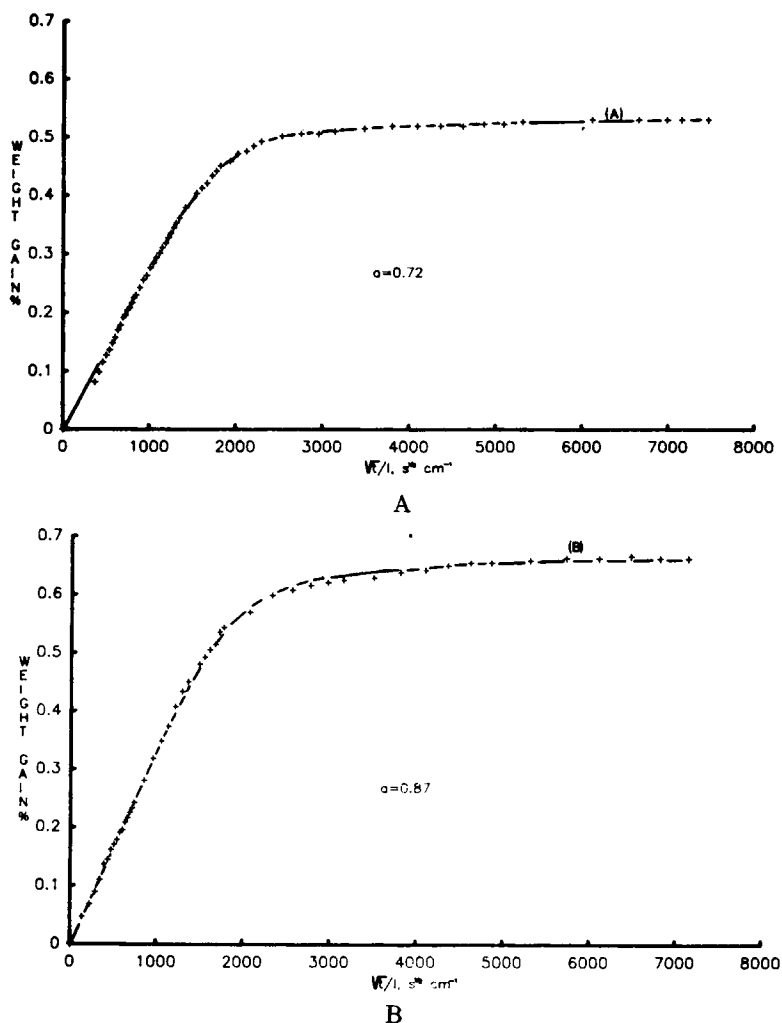
Fig. 4. Water vapor sorption kinetics in 250 μm thick PEEK amorphous film. The full lines represent the Berens–Hopfenberg model [eq. (7)]: (A) $a = 0.72$, $\phi_f = 0.940$, $k = 1.10 \times 10^{-4}$ s^{-1}, $D = 5.8 \times 10^{-8}$ cm^2/s; (B) $a = 0.87$, $\phi_f = 0.905$, $k = 1.35 \times 10^{-4}$ s^{-1}, $D = 5.8 \times 10^{-8}$ cm^2/s.

smaller because of the reduced amount of sorbed solvent. Moreover, the corresponding slower relaxations were probably not observed in the elapsed experimental time. In our case, the Berens–Hopfenberg model gives an excellent phenomenological interpretation of the results in the high activity experiments. The diffusion coefficients, evaluated by fitting the data points with the Fickian model in the case of low activities and with the Berens–Hopfenberg model in the case of higher activities, are essentially constant over the full range of investigated relative humidities.

Water sorption in epoxy resins below their glass transitions[3, 14, 15] and in some glassy thermoplastic polymers[16-18] exhibits hygrothermal history dependence effects. To test the presence of such effects, we submitted the PEEK samples, after exposure to the maximum water activity, to further sorption experiments at low and medium relative pressures.

These resorption experiments carried out at activity values of 0.3 and 0.6 have shown water uptakes practically equal to those obtained in the first sorption at the same activities, indicating the absence of hysteresis in the sorption isotherm. This can be explained considering that the time elapsed between two successive sorption–desorption experiments was quite long (at least 12 h) if compared with the relaxation time ($1/k$ = 3 h), leaving to the polymer structure the possibility of recovering its original morphology.

The relaxation showed at high activity levels is a modification of polymer network that is reversible because of the low water uptake and the weak interaction between water and polymer macromolecules.

Liquid Water Sorption in Semicrystalline PEEK

The sorption process has been determined to follow the classical Fickian mechanism over the full range of the investigated temperatures. The relative water uptake (M_t/M_∞) at different temperatures is shown in Figure 5 the values of diffusivities are reported in Table I. The water uptake at equilibrium does not vary appreciably with temperature, maintaining a mean value of about 0.48%. To make a comparison between the diffusion coefficients evaluated in the semicrystalline samples and those relative to the amorphous PEEK, we assumed that the crystalline fraction influence may be accounted for by means of a "tortuosity" factor, which is practically coincident with the inverse of the amorphous fraction.[19] Therefore, the following relationship holds:

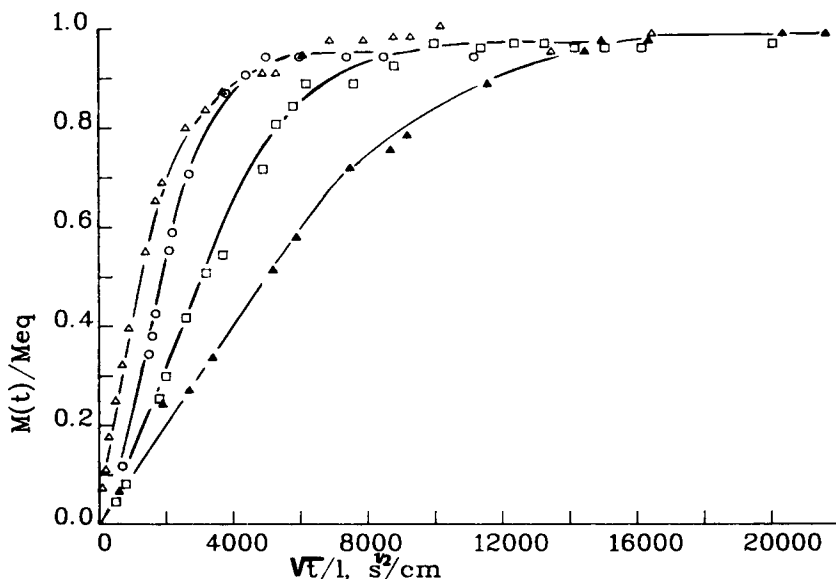$$D_2 = D_1 \cdot (\phi_a)_2/(\phi_a)_1 \qquad (8)$$

Fig. 5. M_t/M_∞ vs. $\sqrt{t}/l$ for liquid water sorption at different temperatures in 2 mm thick semicrystalline (30%) PEEK sheets. The full lines represent the Fickian model using the diffusion coefficients estimated from eq. (1): ($\triangle$) temp = 60°C, D = 35.6 × 10^{-9} cm^2/s; ($\bigcirc$) temp = 40°C, D = 15.2 × 10^{-9} cm^2/s; ($\square$) temp = 20°C, D = 5.3 × 10^{-9} cm^2/s; ($\blacktriangle$) temp = 5°C, D = 1.7 × 10^{-9} cm^2/s.

TABLE I
Diffusion Coefficient at Different Temperatures for Water Sorption in
Semicrystalline (30%) 2 mm Thick PEEK Sheets

T (K)	D (cm^2/s)
278	1.7×10^{-9}
293	5.3×10^{-9}
313	15.2×10^{-9}
333	35.6×10^{-9}

where the subscripts refer to two samples having a different amorphous fraction. This procedure enables us to "normalize" diffusivity values obtained for semicrystalline PEEK, finding the correspondent value relative to the totally amorphous material. At 60°C we found $D = 3.6 \times 10^{-8}$ cm^2/s. "Normalizing" it, we obtain a theoretical value of D for the totally amorphous sample of about 5.2×10^{-8} cm^2/s that is in good agreement with the one evaluated experimentally at 60°C for the amorphous PEEK.

Desorption experiments indicated also in this case a Fickian behavior with diffusivities substantially equal to those calculated for the sorption tests. The absence for the semicrystalline samples of the diffusion–relaxation superposition effect that we found for the amorphous ones can be attributed to the larger value of the sample thickness (2 mm vs 250 μm) and to the partial crystalline nature of the polymer structure.

In fact, in the case of our semicrystalline samples, due to the greater thickness (2 mm), the characteristic time of diffusion ($\theta = l^2/D$) is strongly increased; consequently, the DEB value becomes about 1×10^{-2} ($\ll 1$); we are then in the case of "viscous diffusion" in which the mass transfer is diffusion-controlled and the two mechanisms (molecular diffusion and relaxation) are no more distinguishable.

The activation energy involved in the diffusion process is 10.1 kcal/kmol (Fig. 6). These data agree with the results reported by Grayson and Wolf.[5]
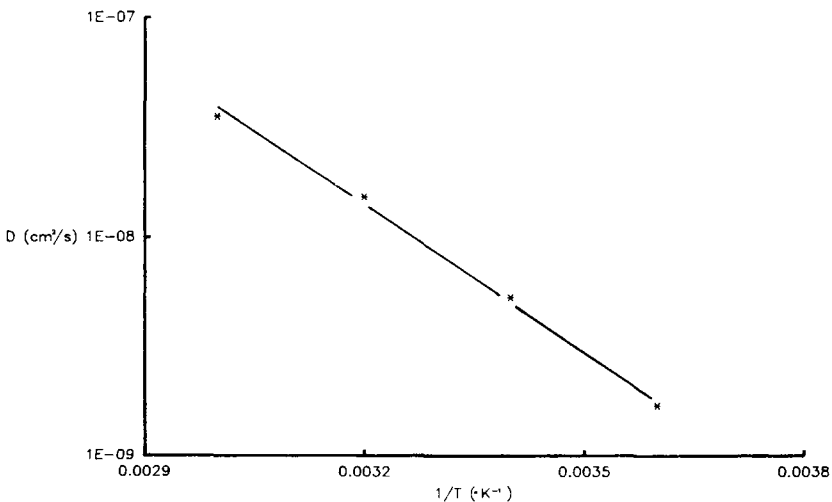

Fig. 6. Arrhenius plot of water diffusion in semicrystalline (30%) 2 mm thick neat PEEK sheets.
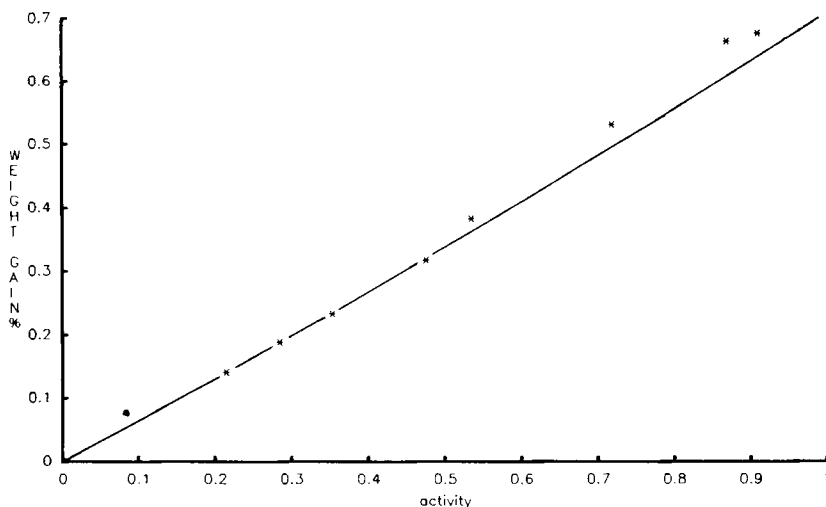
Fig. 7. Water equilibrium uptake for vapor sorption in 250 μm PEEK amorphous film. The full line represents the Flory–Huggins equation [eq. (9)] obtained by best fitting of the low and medium activity data with a value of $\chi_s = 3.80$.

SORPTION EQUILIBRIA

In Figure 7 the sorption isotherm at 60°C relative to the amorphous samples is shown. The results can be interpreted in terms of the Flory–Huggins equation.

$$\ln a_s = \ln\left(1 - v_p\right) + v_p + \chi_s v_p^2 \tag{9}$$

where a is the solvent activity, v_p is the polymer volume fraction, and χ_s is the solvent–polymer interaction parameter. In the figure the theoretical curve evaluated through eq. (9) is also reported; the χ_s value was calculated using a nonlinear regression of data points relative to the low and medium activities (up to 0.5), using a computer-aided statistical program. The obtained value ($\chi_s = 3.80$) gives the best-fitting curve of the first experimental points but provides a lower uptake value if compared to the experimental values at high activities. This difference can be related to the relaxation process previously discussed.

In the interpretation of the equilibrium value, we have not considered the presence of a Langmuir contribution: The high sample density and the low water uptake let us presume a negligible entity of such sorption mechanism. The sorption data indicate that at $a = 1$ the equilibrium value is close to 0.70%.

For the semicrystalline PEEK immersed in liquid water a mean equilibrium value (0.48%) roughly constant with temperature was observed. If we assume that the crystalline fraction is not capable of sorption, we can calculate the theoretical water uptake relative to the amorphous fraction. The calculated value of water uptake of 0.69% is close to the value we obtained from the data of water vapor sorption of the amorphous samples.

After the sorption tests both types of samples were analyzed with the DSC and the results indicated no significant differences with the virgin ones (excluding a 2°C depression of the glass transition temperature).

MENSITIERI ET AL.

CONCLUSION

In this work the moisture and liquid water sorption behavior of both amorphous and semicrystalline PEEK has been investigated. The experiments carried out at low water vapor activity indicated a purely Fickian behavior of penetrant diffusion in amorphous PEEK films for the elapsed experimental times. At higher activities the amorphous samples showed an anomalous diffusion mechanism successfully interpreted by means of a linear superposition of a Fickian diffusion process and a first-order relaxation term. Using this approach, the true diffusion coefficient has been evaluated for high activities, showing that it has a roughly constant value over the entire range of investigated conditions.

The equilibrium sorption data at high water activities showed a deviation from the Flory–Huggins curve obtained fitting the lower activities data points. This effect is connected with the relaxation process exhibited in the kinetic diffusion curves. The absence of hysteresis effects in equilibrium resorption experiments suggests that the resin morphology is not altered by sorption–desorption–resorption cycles.

The liquid water sorption experiments performed on semicrystalline PEEK films exhibited a purely Fickian behavior. The absence of the sorption anomalies encountered in the amorphous specimens is attributed to the greater sample thickness and, to some extent, to the partial crystalline nature of the polymer structure.

The water uptake values obtained for both amorphous and semicrystalline PEEK confirm the good moisture and liquid water resistance of this kind of high performance thermoplastic polymer.

References

1. D. J. Blundell and B. N. Osborn, *Polymer*, **24**, 953 (1983).
2. C. Carfagna, E. Amendola, A. D'Amore, and L. Nicolais, *Polym. Eng. Sci.*, to appear.
3. A. Apicella, R. Tessieri, and C. De Cataldis, *J. Membr. Sci.*, **18**, 211 (1984).
4. E. J. Stober, J. C. Seferis, and J. D. Keenan, *Polymer*, **25**, 1845 (1984).
5. M. A. Grayson and C. J. Wolf, *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 31 (1987).
6. H. B. Hopfenberg and H. L. Frisch, *J. Polym. Sci, Polym. Phys. Ed.*, **7**, 405 (1969).
7. J. S. Vrentas, C. M. Jarzebski, and J. L. Duda, *AIChE J.*, **21**, 894 (1975).
8. A. R. Berens, *Polymer*, **18**, 697 (1977).
9. A. R. Berens and H. B. Hopfenberg, *Polymer*, **19**, 489 (1978).
10. D. J. Blundell, D. R. Beckett, and P. H. Willcocks, *Polymer*, **22**, 704 (1981).
11. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, London, 1975.
12. C. J. Patton, R. M. Felder, and W. J. Koros, *J. Appl. Polym. Sci.*, **29**, 1095 (1984).
13. T. C. Wong and L. J. Broutman, *Polym. Eng. Sci.*, **25**, 521 (1985).
14. A. Apicella, L. Nicolais, G. Astarita, and E. Drioli, *Polym. Eng. Sci*, **21**, 18 (1981).
15. J. A. Barrie, P. S. Sagoo, and P. Johncock, *Polymer*, **26**, 1167 (1985).
16. D. J. Enscore, H. B. Hopfenberg, V. T. Stannett, and A. R. Berens, *Polymer*, **18**, 1105 (1977).
17. D. J. Enscore, H. B. Hopfenberg, and V. T. Stannett, *Polym. Eng. Sci.*, **20**, 102 (1980).
18. H. Ghavamikia and D. A. Blackadder, *Polymer*, **21**, 901 (1980).
19. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 2171 (1978).