S0032-3861(96)00334-5

Polymer Vol. 37 No. 25, pp. 5627-5637, 1996

0032-3861/96/$15.00+0.00

Diffusion of methylene chloride and tetrahydrofuran in amorphous poly(ether ether ketone)

Hélène Cornélis and Ronald G. Kander*
Materials Science and Engineering Department, 213 Holden Hall, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0237, USA
(Received 13 November 1995; revised 15 February 1996)

The diffusion of methylene chloride and tetrahydrofuran in amorphous poly(ether ether ketone) (PEEK) films was studied by the following method. A specimen was immersed in the solvent, the reaction was stopped by immersing the specimen in liquid nitrogen, the dried specimen was finally fractured into two pieces, one for observation under scanning electron microscope and the other for thermal analysis by differential scanning calorimetry. As the solvent was allowed more time to penetrate into the film, the fracture surfaces showed distinct solvent diffusion fronts that increased in thickness and the d.s.c. curves displayed crystallization exothermic peaks whose areas decreased, showing the solvent-induced crytallization (SINC) process. SINC was then analysed in term of the diffusion process using the Zachmann and Konrad theory. The SINC process was found to be solvent-diffusion controlled. Copyright © 1996 Elsevier Science Ltd.

(Keywords: diffusion; PEEK; crystallization)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-performance semi-crystalline thermoplastic used in composite and aerospace applications, where exposure to various solvents may occur. Although the chemical resistance of PEEK is relatively good, recent studies have shown that PEEK can be swollen by either benzene derivatives (e.g., tetrahydrofuran) or small chlorinated hydrocarbons (e.g., 1,1,2,2-tetrachloroethane and methylene chloride), which can cause plasticization and further crystallization[1-9].

This paper reports the results of diffusion experiments on amorphous PEEK films with two good solvents (i.e., methylene chloride and tetrahydrofuran) which have already been found to plasticize and induce crystallinity in PEEK. Both the diffusion- and the solvent-induced crystallization (SINC) phenomena are studied through the following experiment: a specimen was exposed to a solvent for a certain amount of time and the diffusion process stopped by immersing the sample in liquid nitrogen. This type of experiment permits the observation of the diffusion front of the solvent and of the SINC process, which is analysed using the Zachmann and Konrad theory.

THEORETICAL BACKGROUND

Theoretical models have been developed to predict the development of crystallinity with time. The overall crystallization kinetics of polymers is commonly described by the familiar Avrami expression[10,11]

$$1 - X(t) = \exp(-Kt^n) \qquad (1)$$

where X is the fraction of the total volume of the starting material that has undergone crystallization and K is the crystallization rate constant containing the crystallite growth rate and either the nucleation density for heterogeneous nucleation or nucleation rate for homogeneous nucleation. The Avrami equation is a simple model for one mode of crystallization. The time constant n (also called the Avrami exponent), which theoretically takes on integer values from 1 to 4, serves to indicate the geometry of the growing crystalline entities (rod, disk, or spherulite growth from simultaneous or sporadic nucleation) and the time dependence of the nucleation process involved in the crystallization. Half-integer values for n are also possible for crystallizing systems with severe diffusional limitations with respect to the mobility of the macromolecules in the melt.

The Avrami analysis has been used for solvent-induced crystallization, but it must be modified. For SINC, the polymer is not entirely in the same state relative to the crystallization temperature at the same time (e.g., some volume elements have their T_g above T_c and some other volume elements have their T_g below T_c), as a given polymer volume element crystallizes after being penetrated by the distinct front of solvent advancing inward from the outer polymer surface. The varying crystallization time scale for each volume element must therefore be considered in the calculation of the overall fractional volume of crystallized polymer at any given time.

---

*To whom correspondence should be addressed

Zachmann and Konrad[12] applied a modified Avrami-type analysis to the case of solvent-induced crystallization. The solvent which is capable of inducing crystallization in a polymer film (thickness $= 2a$) is assumed to penetrate the polymer as a distinct advancing front. This penetration, which is linear with the square root of time (i.e. Fickian diffusion), can be characterized by a rate constant b which is proportional to the diffusivity. Thus, the distance of penetration of the front from the film surface is given by

$$z = b\sqrt{t} \tag{2}$$

The polymer volume elements are also assumed to crystallize according to the classic Avrami kinetics, with crystallization rate constant K_∞ associated with the saturation concentration of the penetrant in the polymer, C_∞. Letting

$$z' = \frac{z}{a} \quad t' = \sqrt[3]{K_\infty t}$$

and

$$b'^2 = \frac{b^2}{a^2 \sqrt[3]{K_\infty}}$$

the overall volume fraction of material crystallized in the entire sample $[x(t')]$ can be given by the dimensionless Avrami-type relation

$$x(t') = \int_0^{b'\sqrt{t'}} \left\{1 - \exp\left[-\left(t' - \frac{z'^2}{b'^2}\right)^3\right]\right\} dz' \tag{3}$$

This expression holds for all $b'\sqrt{t'} < 1$. When the diffusion front has reached the center of the film (i.e., $b'\sqrt{t'} = 1$), the entire sample contains the penetrant at concentration c_∞, and Equation (3) must be replaced by

$$x(t') = \int_0^{1} \left\{1 - \exp\left[-\left(t' - \frac{z'^2}{b'^2}\right)^3\right]\right\} dz' \tag{4}$$

Zachmann and Konrad then defined τ_∞ as the crystallization half-time for the conditions $C = C_\infty$ and rate constant K_∞

$$\tau_\infty = \sqrt[3]{\frac{\ln 2}{K_\infty}} \tag{5}$$

and t_E as the time for complete penetration of the film by the newly sorbed penetrant

$$t_E = \frac{a^2}{b^2} \tag{6}$$

The parameter t_E/τ_∞ measures the characteristic time scale for diffusion compared to the characteristic time for crystallization, and it is equal to

$$\frac{t_E}{\tau_\infty} = \frac{1.14}{b'^2} \tag{7}$$

The parameter determines the crystallization time scale by taking into account the moving front of solvent which induces crystallization. When t_E/τ_∞ is very small, diffusion takes place extremely rapidly compared with crystallization. The entire sample crystallizes as a whole with rate constant K_∞ and each volume element experiences the same time-scale for crystallization (i.e., there are no diffusional limitations). Conversely, when t_E/τ_∞ is very large, each volume element crystallizes fully as soon as the diffusion front passes through it, it is a completely diffusion-limited overall crystallization kinetic, and the measured crystallinity should proceed with a $\sqrt{t}$ dependence. Zachmann and Konrad have numerically integrated equations (3) and (4) for various values of t_E/τ_∞ to demonstrate the effect of the variation of this parameter on the observed time dependence of the overall crystallization process. For PET, the value $t_E/\tau_\infty \geq 100$ appears to be the critical value beyond which diffusional limitation is in evidence.

In order to develop this analysis, Zachmann and Konrad made several assumptions, such as a constant density upon crystallization, no effect of the penetrant on the overall sample dimensions, a Fickian diffusion of the penetrant into the polymer, and no gradient in liquid concentration at the advancing front–dry polymer interface. If these assumptions were relaxed to improve the generality of this approach, the analysis would become far more complicated[10]. One should be aware of these limitations when using this analysis.

EXPERIMENTAL

Materials

The PEEK powder was purchased from ICI (Victrex®, grade 150PF). It has a reported intrinsic viscosity of 0.15, with weight and number average molecular weights of 33 500 and 11 700, respectively. The PEEK powder is a commercial grade, which may contain additives, such as stabilizers for processing (oxidation) and for use (u.v.. stabilizers).

The methylene chloride and tetrahydrofuran (both h.p.l.c. grade) were purchased from Fisher.

Film preparation

The PEEK powder was compression-moulded between metal plates using a Carver laboratory hot press at 385°C for 5 min. A mould release agent (Frekote 800-NC from Dexter Corporation) was used to hinder the PEEK melt from sticking to the metal plates and the Kapton sheets. The PEEK melt was quenched in ice water to obtain approximately 0.3 mm thick amorphous films. These amorphous films were physically aged in a 135°C oven (8°C below the glass transition temperature of PEEK) for 66 h. Absence of orientation in the amorphous film was verified by wide-angle X-ray scattering (WAXS) with a CuK_α radiation source ($\lambda = 1.54$ Å) and a Warhus camera. Two broad amorphous haloes were obtained in both directions (perpendicular and parallel to the surface of the film) suggesting that no orientation was present in the amorphous PEEK film. The effect of the mould release agent on the solvent diffusion in the specimens was minimized by mildly polishing the sample surface using a silicon carbide sandpaper (600 grit), which also minimized any damage to the surface of the films.

Dynamic solvent uptake measurements

The dynamic solvent uptake measurements consisted of placing a piece of the PEEK film in a solvent and periodically removing the specimen from the solvent and weighing it using a Mettler AE30 millibalance. A sample was placed in a scintillation vial (total volume of 20 ml)

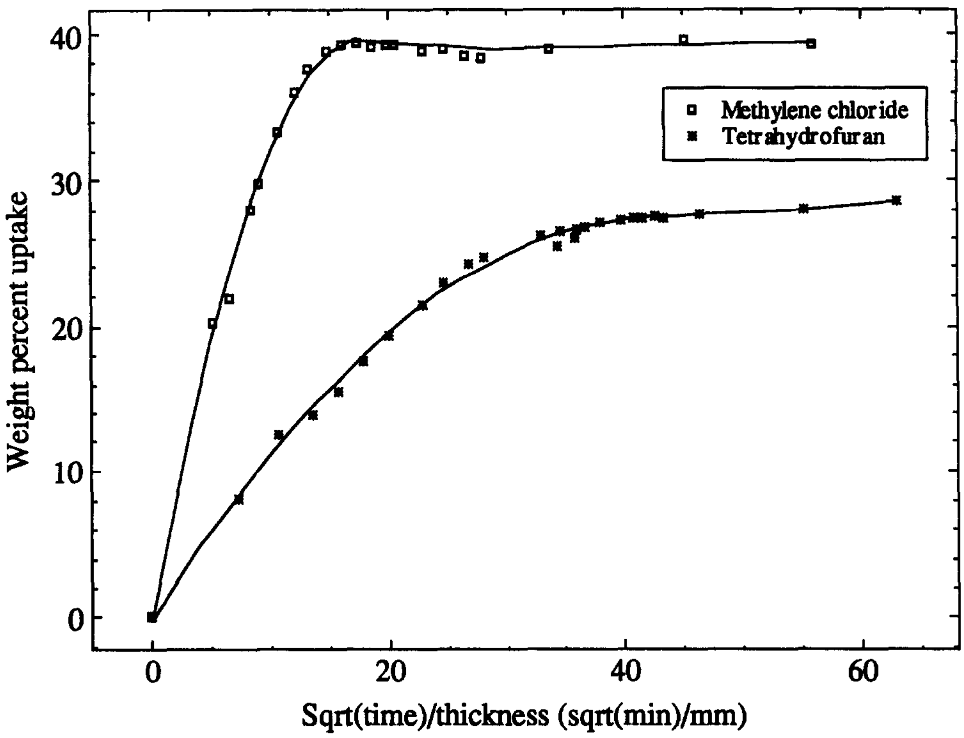


Figure 1 Dynamic solvent uptakes of methylene chloride and tetrahydrofuran in amorphous PEEK

with methhylene chloride or tetrahydrofuran and was stored at room temperature during the entire period of experimentation. Before each weight measurement, the surface of the sample was carefully wiped to eliminate any residual solvent. When the measurements were completed, the sample was promptly put back in its scintillation vial; the entire process took 20–30 s. The dynamic solvent uptake results are shown in conventional Fickian plots (*Figures 1, 4b, 5b, 8b* and *9b*). The weight per cent uptake is plotted against the square root of time over the thickness of the specimen. The experimental error for the weight uptake is 0.5 wt%.

Diffusion experiment

The diffusion of solvents in the amorphous PEEK films was studied by immersing a piece of the amorphous PEEK film (1 cm × 1 cm × 0.33 mm) in the chosen solvent (i.e., methylene chloride and tetrahydrofuran) for times ranging from 1 to 30 min, at approximately 21°C. The diffusion of the solvent in the specimen was stopped by immersing the partly swollen specimen in liquid nitrogen. The specimen was then dried under vacuum using the desorption method described below. Finally, the sample was fractured in liquid nitrogen to produce two pieces, one for examination in the scanning electron microscope (SEM) and the other for differential scanning calorimetry (d.s.c.) measurements.

Desorption method

The technique used to desorb the partly swollen PEEK samples consisted of first putting the samples in a desiccator under vacuum at approximately 21°C until equilibrium in the weight loss was recorded and then placing the partly desorbed samples in a vacuum oven at 70°C, which is above the boiling point of methylene chloride and tetrahydrofuran (i.e., $T_b = 40°C$ and 65.5°C, respectively), but far below T_g of PEEK (143°C). Therefore, this technique permits drying of the samples without inducing further crystallization or other structural changes.

Some residual solvent (about 3–4% residual weight) remained in the structure even after equilibrium in the weight loss was recorded at 70°C. This residual solvent would leave the structure if drying was performed at a temperature above T_g of the polymer. However, this high temperature would permit further crystallization to occur, which would interfere with the subsequent analysis.

Scanning electron microscopy

An International Scientific Inc. (SX 40) SEM with a voltage of 20 kV was used to observe the solvent-exposed samples. The samples were first dried then their fracture surfaces were sputtered with gold to create a uniform coating and to prevent the sample from charging during the SEM observation. Micrographs of the fracture surfaces were then taken and analysed.

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) runs were performed with a Mettler TA30000 DSC30 using 5–20 mg samples placed into a d.s.c. pan. The d.s.c. pan was heated from 100°C to 400°C at a rate of 10°C min^{-1}. The solvent-induced crystallization phenomenon was observed as the area under the crystallization peak grew smaller and smaller with increasing solvent diffusion time. For clarity in presenting d.s.c. data, the d.s.c. curves were shifted on the y-axis (i.e., heat flow axis) and not values on the y-coordinates are given.

RESULTS AND DISCUSSION

Figure 1 gives the Fickian plots (i.e., solvent uptake vs the square root of time over the thickness of the specimen) obtained through the dynamic solvent uptake measurements for both methylene and chloride and tetrahydrofuran. The absorption of methylene chloride is much faster

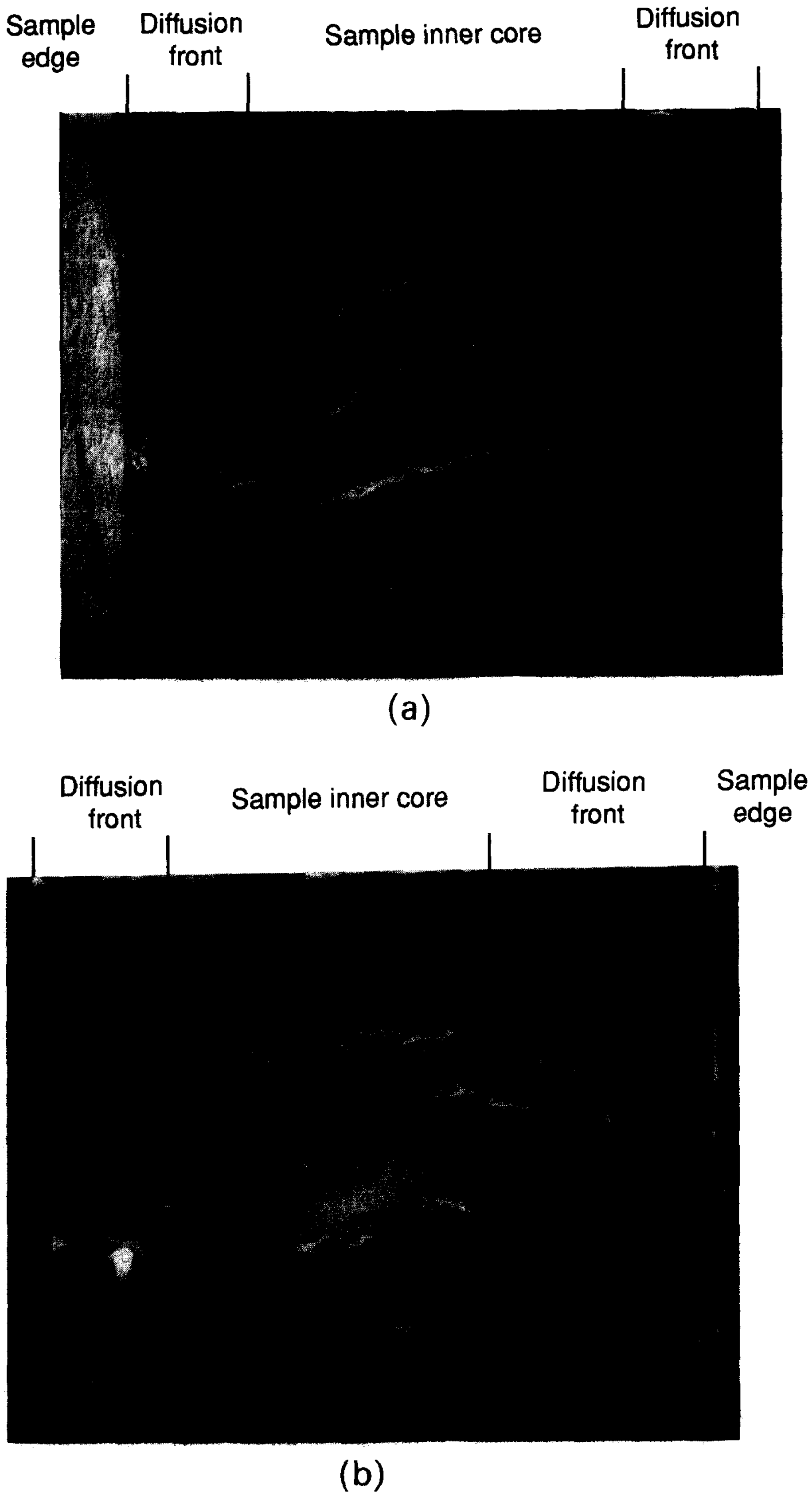
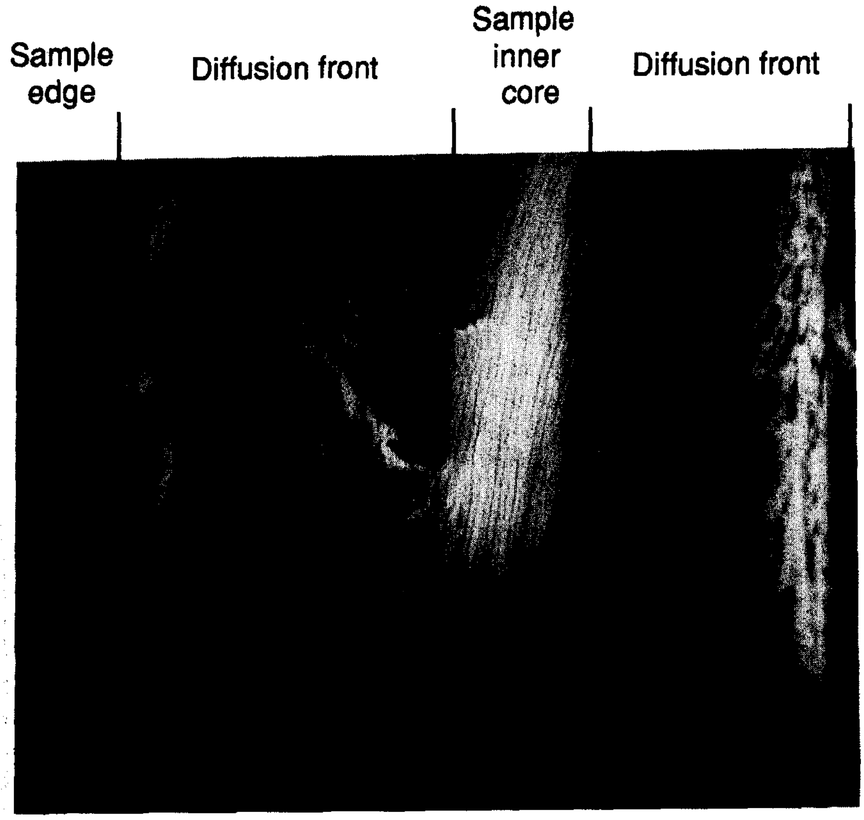
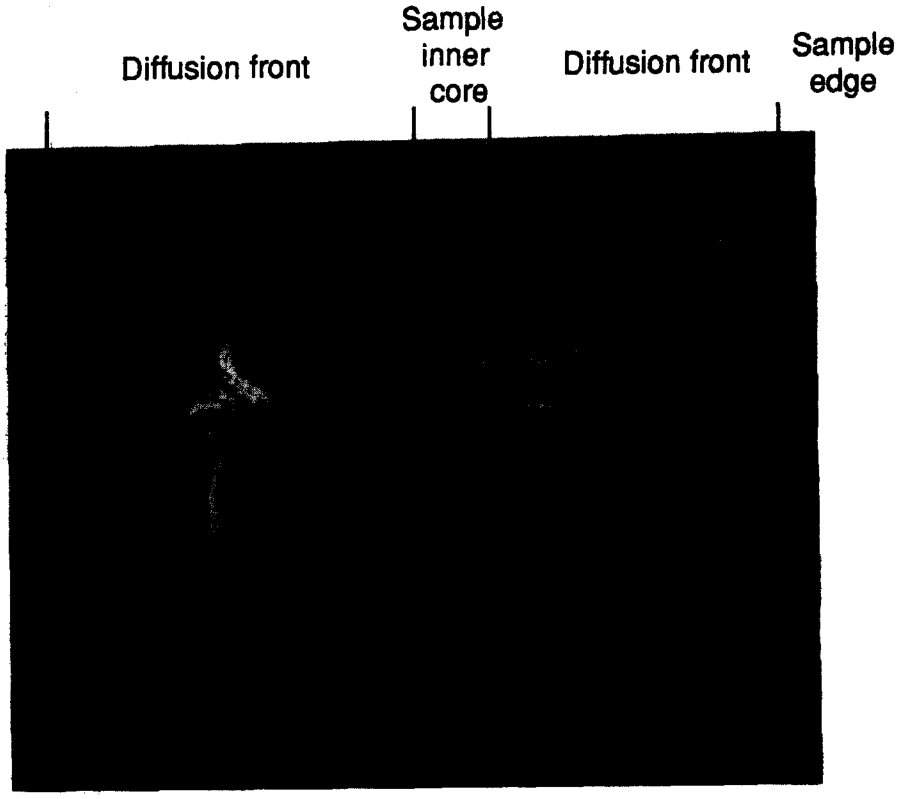


Figure 2 Micrographs presenting fracture surfaces of amorphous PEEK samples where methylene chloride was allowed to diffuse for (a) 1, (b) 3, (c) 8 and (d) 10 min

than that of tetrahydrofuran: the respective diffusion coefficients (obtained in the first part of the Fickian plots) are 1.37×10^{-3} cm^2 s^{-1} and 1.27×10^{-4} cm^2 s^{-1} and the respective times for a 0.3 mm thick PEEK sample to reach equilibrium are approximately 30 min and 90 min. Moreover, the amount of solvent absorbed by the film is greater in the case of methylene chloride than in the case of tetrahydrofuran (39.0% and 28.0%, respectively).



(c)



(d)

Figure 2 (*Continued*)

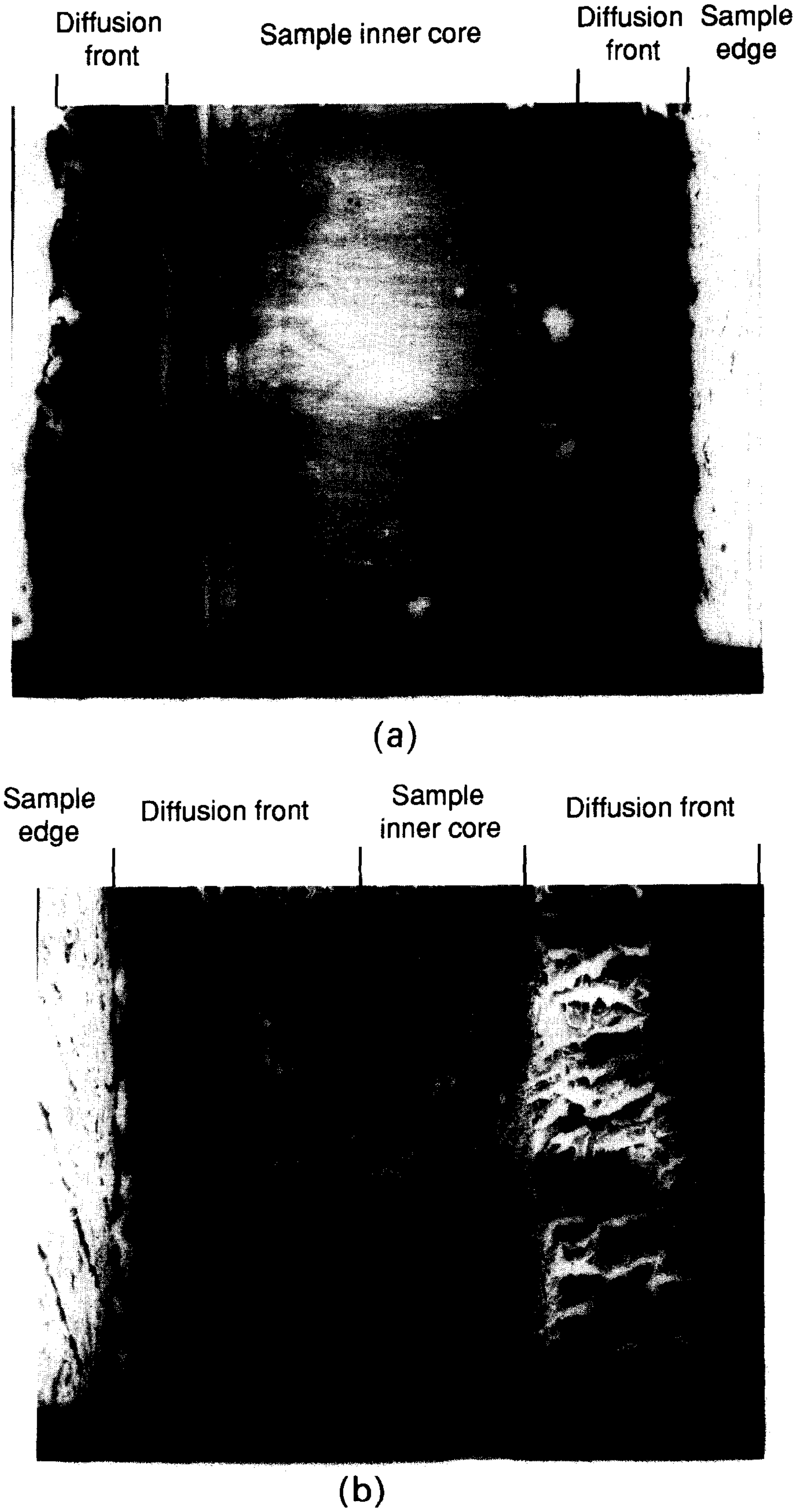


Figure 3 Micrographs presenting fracture surfaces of amorphous PEEK samples where tetrahydrofuran was allowed to diffuse for (a) 5, (b) 15, (c) 25 and (d) 30 min

The methylene chloride/PEEK system was further studied by allowing the solvent to diffuse into the polymer for periods of time between 1 and 18 min with a time increment of 1 min between each time period. The tetrahydrofuran/PEEK system was further studied by allowing the solvent to diffuse into the polymer for periods of time between 5 and 50 min with a time increment of 5 min between each time period. These periods correspond to the most appropriate times for experimental observations of solvent

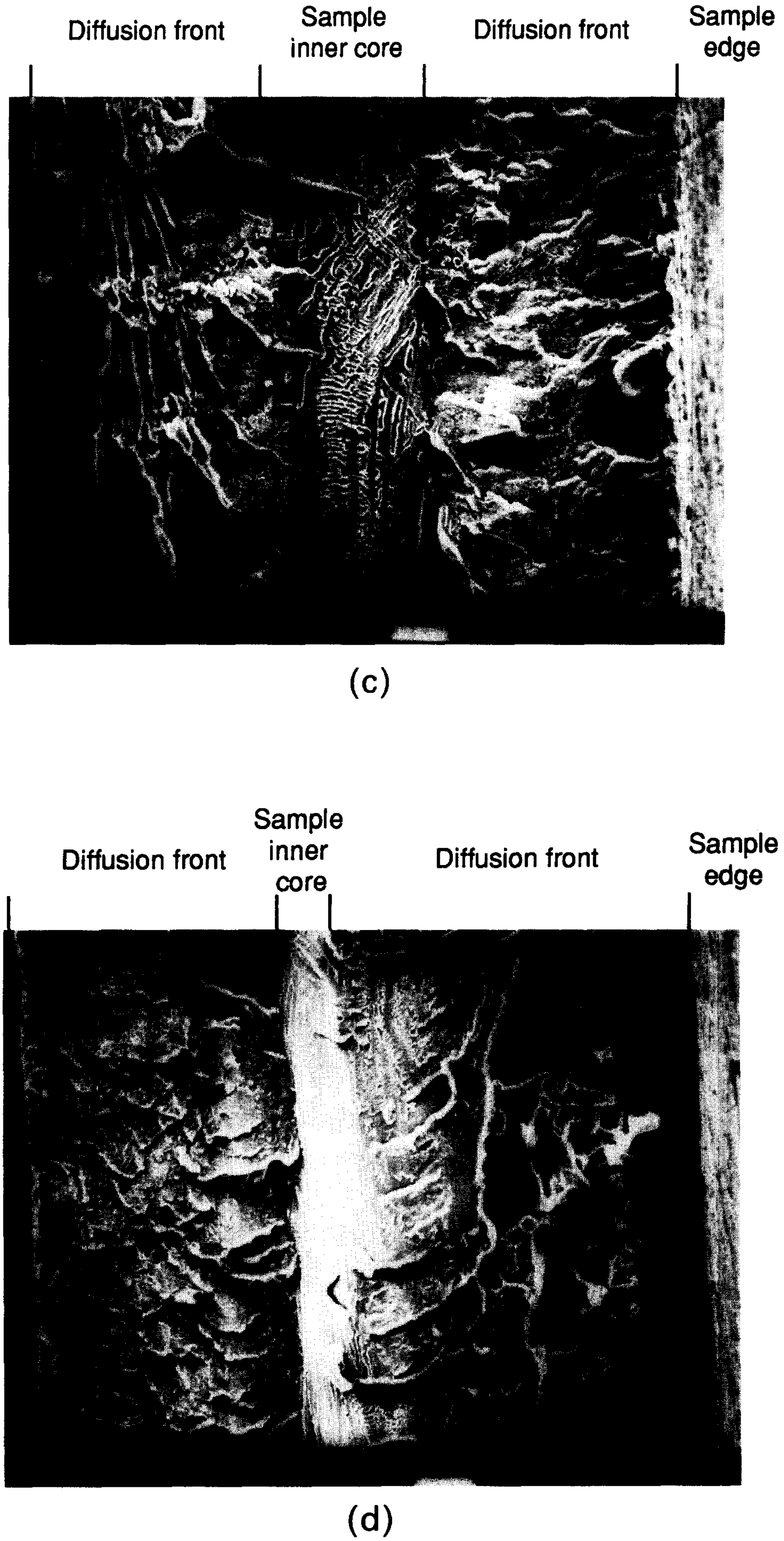


Figure 3 (*Continued*)

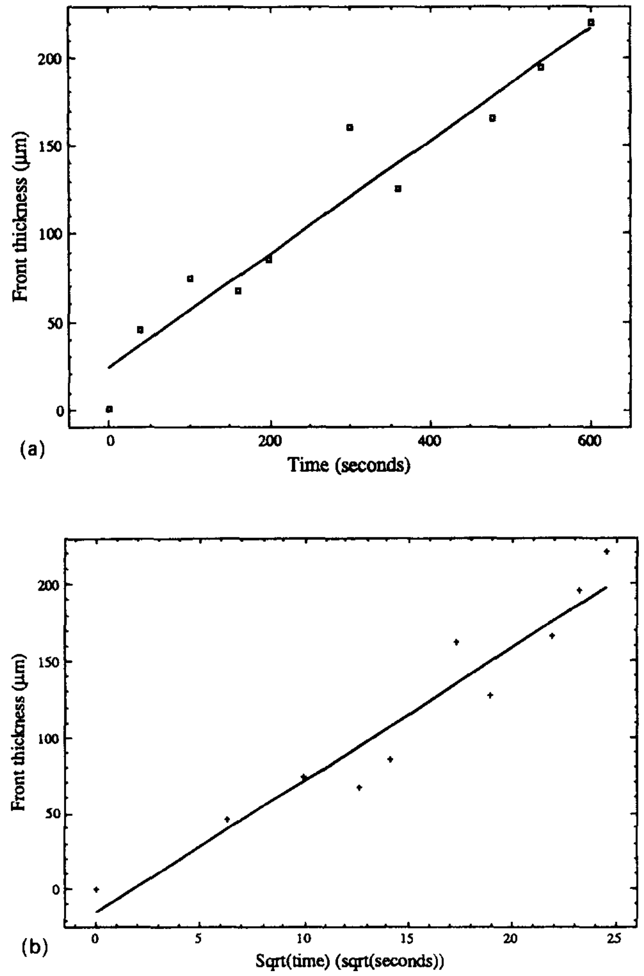


Figure 4 Variation of front thickness of methylene chloride in amorphous PEEK as observed on the fracture surfaces. (a) Front thickness vs time (i.e., Case II diffusion); (b) front thickness vs square root to time (i.e., Fickian diffusion)

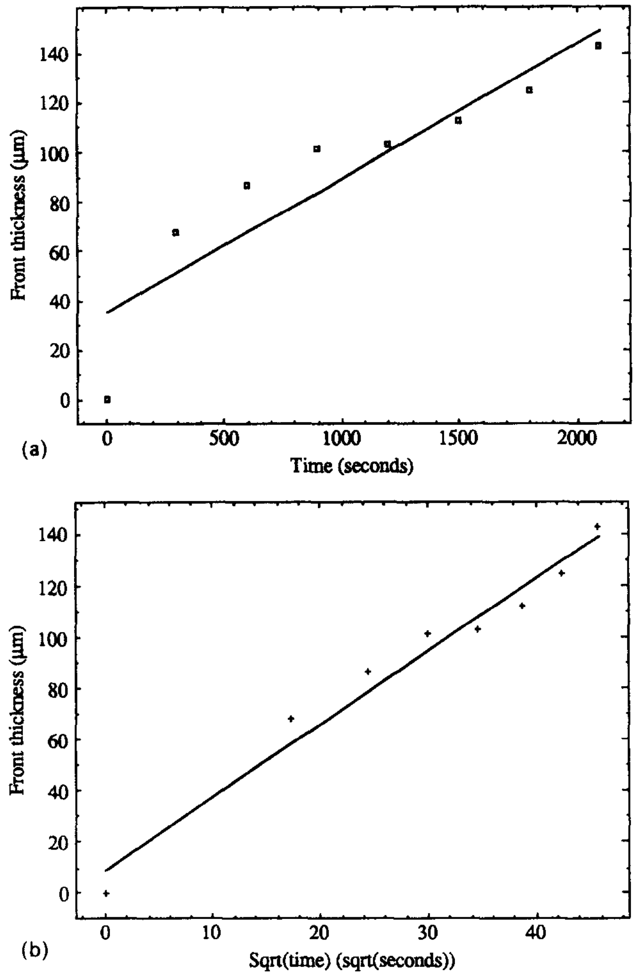


Figure 5 Variation of front thickness of tetrahydrofuran in amorphous PEEK as observed on the fracture surfaces. (a) Front thickness vs time (i.e., Case II diffusion); (b) front thickness vs square root to time (i.e., Fickian diffusion)

diffusion (by SEM) and solvent-induced crystallization (by d.s.c.).

The solvent diffusion fronts were observed to meet at the middle of the specimen after 10 min of diffusion for the methylene chloride/PEEK system and after 30 min for the tetrahydrofuran/PEEK system. After these periods of time, no distinct solvent fronts could be distinguished for both systems. The micrographs obtained with the SEM for the methylene chloride/PEEK and tetrahydrofuran/PEEK systems are given in *Figure 2* and *Figure 3*, respectively. These micrographs show fracture surfaces of the partly swollen samples (the thickness of the sample is on the horizontal axis). The diffusion of the solvent occurred from the outer edges of the specimens to the inner core. On *Figure 2* and *Figure 3*, the diffusion front can be observed as the 'plasticized' part on the outer sides of the fracture surfaces ('plasticized' during diffusion of the solvent, but not during the fracture process as it occurred at liquid nitrogen temperature). In both figures, the edges of the specimen and also the boundaries of the solvent diffusion front are indicated.

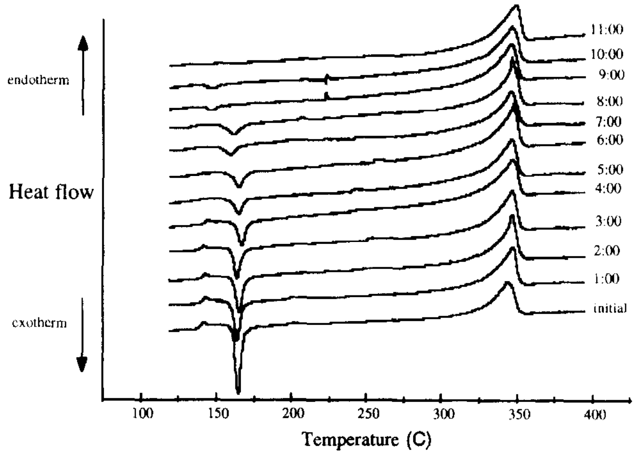


Figure 6 D.s.c. curves of amorphous PEEK films into which methylene chloride was allowed to diffuse for the indicated periods of time (in minutes)

From micrographs similar to those shown in *Figure 2* and *Figure 3*, the thickness of the diffusion fronts for the methylene chloride/PEEK and tetrahydrofuran/PEEK systems can be plotted against time (i.e., Case II diffusion) or the square root of time (i.e. Fickian diffusion). This can be done up to the merging of the two solvent diffusion fronts (i.e., 10 min for methylene chloride and 30 min for tetrahydrofuran). These plots are shown in *Figure 4* and *Figure 5* along with the straight line obtained by linear regression. For the methylene chloride/PEEK system, the correlation coefficients are 0.965 and 0.961 for the Case II diffusion and Fickian diffusion plots, respectively,

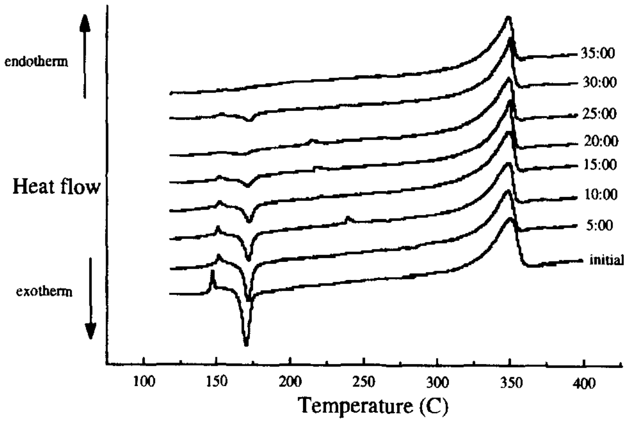


Figure 7 D.s.c. curves of amorphous PEEK films into which tetrahydrofuran was allowed to diffuse for the indicated periods of time (in minutes)

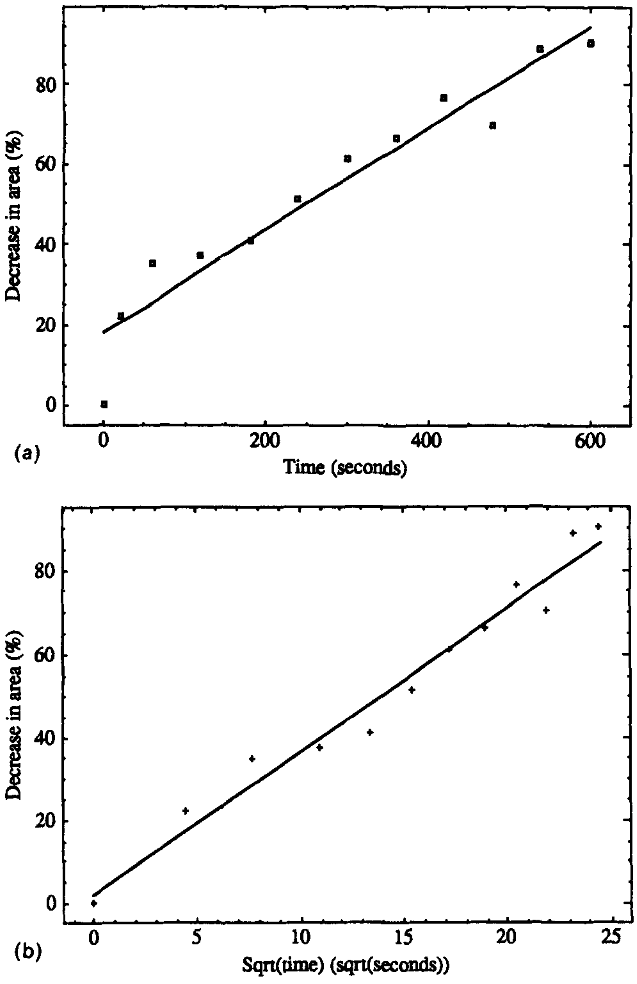


Figure 8 Decrease in area of the crystallization peaks from the d.s.c. curves of amorphous PEEK exposed to methylene chloride for different periods of time vs (a) time and (b) square root of time

whereas, in the case of the tetrahydrofuran/PEEK system, the correlation coefficients are 0.910 and 0.976, respectively. As suggested by the correlation coefficients, the level of fitting of the experimental points with the linear regression is similar for the Case II diffusion and Fickian diffusion, in the case of the diffusion of methylene chloride in amorphous PEEK. Therefore, no distinction between these two diffusion cases could be made for this system. This inability to distinguish between one case or the other is reflected in the literature[1,7,13] as both cases have ben used to describe the absorption of methylene chloride in amorphous PEEK. For the tetrahydrofuran/PEEK system, a higher correlation coefficient is obtained for Fickian diffusion than for Case II diffusion, so that it could be assumed that tetrahydrofuran diffuses in amorphous PEEK according to a Fickian law. In the time-scale of interest in this study (i.e., long-term properties of PEEK exposed to one of the solvents), the mode of diffusion of the solvents in PEEK is not essential. Therefore, the

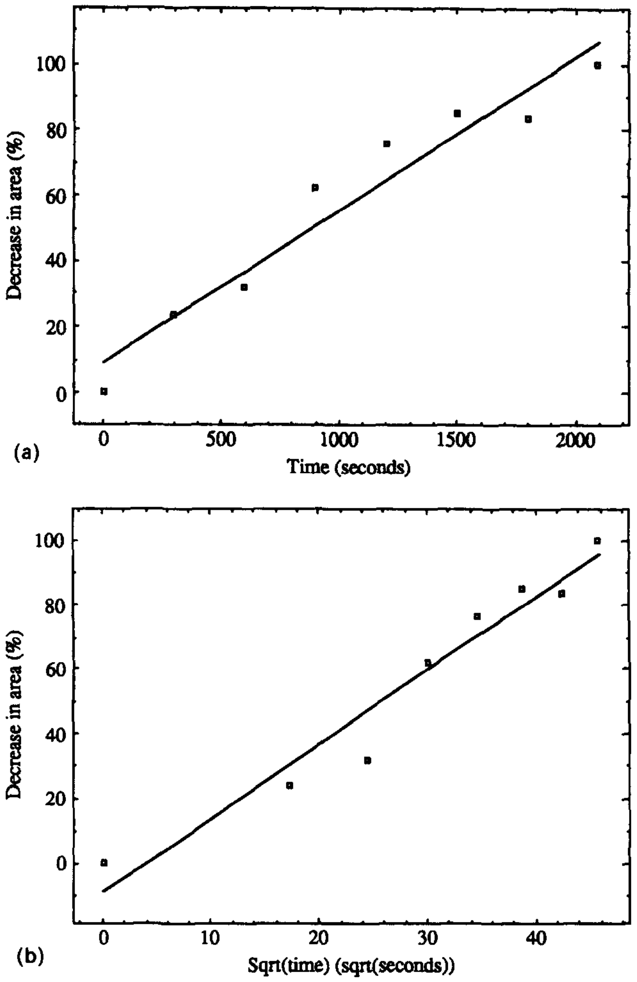


Figure 9 Decrease in area of the crystallization peaks from the d.s.c. curves of amorphous PEEK exposed to tetrahydrofuran for different periods of time vs (a) time and (b) square root of time

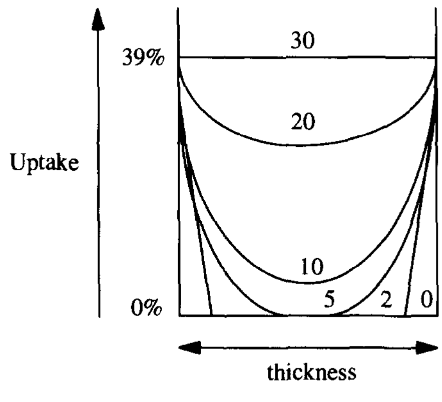


Figure 10 Schematic representation of the diffusion of methylene chloride in an amorphous PEEK film

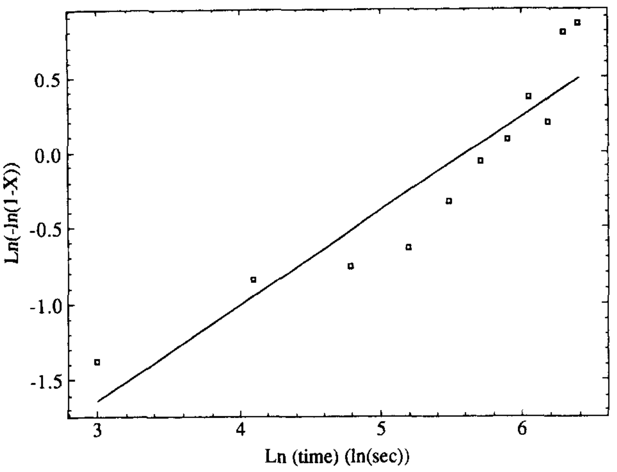


Figure 11 Avrami plot for the methylene chloride/amorphous PEEK system

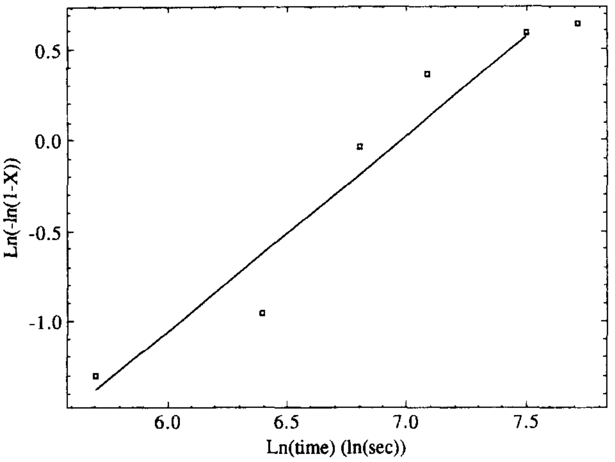


Figure 12 Avrami plot for the tetrahydrofuran/amorphous PEEK system

Fickian diffusion model will be used to describe further the absorption of the methylene chloride and tetrahydrofuran in amorphous PEEK.

The d.s.c. runs obtained for the methylene chloride/PEEK and tetrahydrofuran/PEEK systems are given in *Figure 6* and *Figure 7*, respectively. Note the decrease in the area of the exothermic crystallization peak with time, which is related to the SINC process occurring during the diffusion of the solvents into the polymeric film. This decrease in area can be plotted against time and square root of time, which has been done in *Figure 8* and *Figure 9* for the methylene chloride/PEEK and tetrahydrofuran/PEEK systems, respectively. Linear regression was also applied to the two sets of data for each system. For the methylene chloride/PEEK system, the correlation coefficients are 0.970 and 0.983 for the plots against time and square root of time, respectively, while, for the tetrahydrofuran/PEEK system, the correlation coefficients are 0.969 and 0.973, respectively. For both systems, the correlation coefficients for the plots against square root of time are slightly higher than those for the plots against time. However, if the experimental error is taken into account, no major differences between the two kinds of plot can be made.

If the two plots in *Figure 4* are superimposed with the two plots in *Figure 8* and if the two plots in *Figure 5* are superimposed with the two plots in *Figure 9*, the straight lines from the linear regression almost correspond to one another. Furthermore, the decrease in the area of the crystallization peak from the d.s.c. curves corresponds to the solvent-induced crystallization process and the variation of the front thickness corresponds to the diffusion process. The time it took the methylene chloride and tetrahydrofuran diffusion fronts to reach the middle of the sample, as observed by SEM, also corresponds to the time the SINC process took for both solvents as observed by d.s.c. These observations suggest that, in both systems, the solvent-induced crystallization process is controlled by the diffusion process.

A comparison between the results from the diffusion experiment and the dynamic solvent uptake results also reveals that two processes are involved during the absorption of the solvents in the polymeric films. The methylene chloride diffusion front was observed to reach the middle of a 0.33 mm thick amorphous PEEK sample in less than 11 min, and the tetrahydrofuran diffusion front needed less than 35 min to reach the middle of a 0.3 mm thick amorphous PEEK sample. Conversely, the dynamic solvent uptake measurements showed that equilibrium in the weight uptake of the amorphous PEEK sample was reached in about 30 min when it was exposed to methylene chloride and in about 90 min when it was exposed to tetrahydrofuran (these times are for amorphous PEEK samples with same thicknesses as those used in the diffusion experiments). Therefore, in the first one-third of the equilibrium time, the solvent molecules diffuse through the polymeric film until the diffusion fronts meet in the middle of the specimen, after which time more solvent molecules penetrate the specimen and go into the free volume of the polymer (i.e., they swell the specimen). During the first part of solvent diffusion, the solvent molecules disrupt the intermolecular forces between the macromolecules, resulting in a loosened structure where more and more solvent molecules can fit. Equilibrium in mass uptake occurs when the structure is saturated with solvent molecules and balance between solvent-induced crystallinity and swollen amorphous phase is reached. *Figure 10* gives a schematic representation of the diffusion of methylene chloride in the amorphous PEEK film. In *Figure 10*, the level of methylene chloride molecules present in the structure is presented by the curved lines for different times (given in minutes). The amount of solvent is higher near the surfaces of the film than in the inner core until equilibrium in the weight uptake is reached, at which

Table 1 Evaluated n, K, b, r_E, τ, and t_E/τ_∞ for the methylene chloride/amorphous PEEK (i.e., CH_2/Cl_2/PEEK) and tetrahydrofuran/amorphous PEEK (i.e., THF/PEEK) systems

	n	K (s^{-3})	b ($m\,s^{-1}$)	t_E (s)	τ (s)	t_E/τ_∞
CH_2/Cl_2/PEEK	0.63	2.97×10^{-2}	8.65	363.86	2.86	127.22
THF/PEEK	1.08	5.3×10^{-4}	2.86	3328.40	10.94	304.27

time the solvent molecules are present in equal amount in the entire film.

The SINC process by methylene chloride and tetrahydrofuran in amorphous PEEK was shown to occur as diffusion of the solvents proceeded in the polymeric film, that is the SINC process is diffusion controlled. Assuming that the diffusion of methylene chloride and tetrahydrofuran in the amorphous PEEK films can be described by Fickian law, the SINC kinetics can be described as a function of diffusion mechanism by applying the Zachmann and Konrad[12] theory presented earlier.

Using the Fickian plots showing the variation of front thickness and also the plots showing the decrease in area of the crystallization peaks as a function of the square root of time, one can evaluate the parameter t_e/τ_∞, which determines the crystallization time scale.

First, the crystallization rate constant K_∞ can be evaluated through the construction of an Avrami plot. Using the plots showing the d.s.c. curves of amorphous PEEK films into which a solvent was allowed to diffuse for certain amounts of time (i.e., *Figure 6* for methylene chloride and *Figure 7* for tetrahydrofuran), one can build Avrami plots. The area under the crystallization peaks of the initial sample corresponds to the fraction of crystallizable material in the sample; let this fraction of crystallizable material be equal to 1. The area under the crystallization peaks for the solvent-exposed samples corresponds to the total fraction of crystallizable material minus the amount of solvent-induced crystallized material (i.e., area $= 1 - X$, where X is the amount of crystallized material). Plotting $\ln(-\ln(1-X))$ against $\ln(t)$, where t is the time (in seconds) the solvents have been allowed to diffuse into the amorphous film, gives the Avrami plots for both systems, which are given in *Figures 11* and *12* for methylene chloride and tetrahydrofuran, respectively. From these Avrami plots, the value of both the Avrami exponent n and the crystallization rate constant K can be evaluated and are given in *Table 1*. Note that the values of the Avrami coefficient n suggest that the crystallinity is one-dimensional in both systems. This linear crystallization was observed by experiment. A thin amorphous PEEK film was produced between two glass microscope slides by melting a small amount of PEEK powder above its melting temperature in the hot stage and quenching the melt in ice-water. Drops of methylene chloride were then put around the sample and the diffusion of the solvent into the amorphous film was observed under the optical microscope. The diffusion front of methylene chloride was found to induce linear crystallization in the amorphous PEEK film. This linear crystallization contrasts with the spherulitic morphology of other solvent-crystallized polymers observed in the literature[10,14,15]. Assuming that crystallization kinetics described by the d.s.c. curves correspond to the crystallization kinetics at saturation concentration, the value of K_∞ is equal to the value of K.

Second, the rate constant b, which is proportional to diffusivity, can be evaluated by considering the plots showing the variation of the front thickness with the square root of time (i.e., *Figure 4b* for methylene chloride and *Figure 5b* for tetrahydrofuran). The parameter b is equal to the slope of the straight lines obtained by linear regression and is given in *Table 1* for both systems.

Finally, the two parameters τ_∞ and t_E can be evaluated from equations (5) and (6); we know that the thickness of the amorphous PEEK film used in the diffusion experiment is 0.33 mm, therefore parameter a is 165 μm. The values of t_E, and τ_∞, and t_E/τ_∞ are given in *Table 1* for both the methylene chloride/PEEK and tetrahydrofuran/PEEK systems.

According to Zachmann and Konrad[12], when t_E/τ_∞ is very large (i.e., $t_E/\tau_\infty \geq 100$), the crystallization kinetics are completely diffusion-limited. From *Table 1*, it can be noted that, for both systems, t_E/τ_∞ is higher than 100, so that the SINC process of amorphous PEEK when exposed to methylene chloride and tetrahydrofuran is a diffusion-controlled process, as suggested previously.

CONCLUSIONS

Diffusion experiments were performed with methylene chloride and tetrahydrofuran on amorphous PEEK films. The diffusion front of the solvent was observed for different times in the SEM and the SINC process was observed through d.s.c.. For the methylene chloride/PEEK system, no distinction between Fickian and Case II diffusions was possible, while, for the tetrahydrofuran/PEEK system, Fickian diffusion was considered more plausible than Case II. In both systems, the SINC press was found to be controlled by the diffusion process which was confirmed by use of the Zachmann and Konrad[13] theory. Comparison between the results from the dynamic solvent uptake measurements and those from the diffusion experiments revealed that the solvent diffusion fronts reached the middle of the specimens in only one-third of the time taken for equilibrium of the weight uptake. After the diffusion fronts met, further solvent diffusion took place in the specimens as the solvent molecules go into the loosened structure and swelled the polymer even more.

ACKNOWLEDGEMENTS

The authors acknowledge the National Science Foundation Science and Technology Center for their financial support for this project through the grant #DMR-9120004.

REFERENCES

1 Stober, E. J. and Seferis J. C. *Polym. Eng. Sci.* 1988, **28**(9), 634

2 Stober, E. J. and Seferis J. C. *Polymer* 1984, **25**, 1845

3 Hay, J. N. and Kemmish, D. J. *Polymer* 1988, **29**, 613

4 Mensitieri, G., Del Nobile, M. A., Apicella, A. and Nicolais, L. *J. Mater. Sci.* 1990, **25**(6), 2963

5 Wolf, C. J., Bornmann, J. A., Grayson, M. A. and Anderson, D. P. *J. Polym. Sci. Part B Polym. Phys.* 1992, **30**, 251

6 Arzak, A., Eguiazabal, J. I. and Nazabal, J. *J. Mater. Sci.* 1993, **28**, 3272

7 Del Bobile, M. A., Nesitieri, G., Netti, P. A. and Nicolais, L. *Chem. Eng. Sci.* 1994, **49**(5), 633

8 Arzak, A., Eguiazabal, J. I. and Nazabal, J. *J. Polym. Sci. Part B Polym. Phys.* 1994, **32**, 325

9 Stuart, B. H. and Williams, D. R. *Polymer* 1994, **35**(6), 1326

10 Makarawicz, P. J. and Wilkes, G. L. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**(9), 1559

11 Hiemenz, P. C. in 'Polymer Chemistry', Marcel Dekker, Inc., New York and Basel, 1984, Chapter 4

12 Zachmann, H. G. and Konrad, G. *Makromol. Chem.* 1968, **118**, 189

13 Mensitieri, G., Del Nobile, M. A., Apicella, A. and Icolais, L. *Polym. Eng. Sci.* 1989, **29**(24), 1786

14 Desai, A. B. and Wilkes, G. L. *J. Polym. Sci. Symp.* 1974, **46**, 291

15 Makarewicz, P. J. and Wilkes, G. L. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1529