The permeation of oxygen through drawn films of poly(ether ether ketone)

G. A. J. Orchard and I. M. Ward*
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK
(Received 24 September 1991; revised 27 January 1992)

The effect of drawing on the oxygen permeability of poly(ether ether ketone) films has been examined. Sample characterization by density and refractive index measurements indicates that the two-fold reduction observed in passing from the amorphous isotropic to the highly drawn state is only partly explained by crystallinity increases and that molecular orientation shown by birefringence is also important.

(Keywords: drawing; PEEK; permeability; birefringence; crystallinity)

INTRODUCTION

The gaseous permeability of a number of polymers has been shown to be considerably affected by the structural changes caused by drawing[1]. While it has been generally established that the gas is confined mainly to the amorphous or disordered regions[2,3], the magnitude of the effect is determined by the details of the structural modifications resulting from the processing. Polyethylene has been found to show a large reduction in permeability which is attributed to dramatic changes in structure and morphology[4]. The much smaller effects observed with poly(ethylene terephthalate) (PET) have been related to changes in molecular conformation[5]. In the present paper, measurements of oxygen permeability are reported for uniaxially drawn poly(ether ether ketone) (PEEK) films.

EXPERIMENTAL

Sample preparation

The PEEK polymer feedstock was supplied by ICI plc in the form of transparent sheets nominally 125 μm thick. Dumb-bell shaped samples of gauge length 56 mm $\times$ 75 mm wide were cut from the sheet with a template. These samples were drawn on an Instron tensile testing machine in a hot air oven at 150°C and 50 mm min^{-1} to a range of draw ratios as shown in *Table 1*. The draw ratios were determined from the final spacing of parallel inked lines marked on the initial samples perpendicular to the draw direction at 2 mm intervals.

When it is drawn, PEEK shows changes in both crystallinity and orientation. To characterize these changes, measurements were made of the densities and the refractive indices of the samples.

Density

Density measurements were made with a water-based density column formed from solutions of potassium iodide at two concentrations. As can be seen in *Table 1*, the density values are in the range of 1.26–1.29.

Refractive indices

The refractive indices of the drawn PEEK differ appreciably for the draw direction and the transverse direction in the plane of the sheet. The refractive indices in the transverse direction and those perpendicular to the surface were measured with a Bellingham & Stanley Abbe refractometer fitted with a polarizing analyser. The samples were suitably oriented with the transverse direction perpendicular to the plane of incidence and α-bromonaphthalene was used as the contact liquid on the prism face. The range of refractive indices which can be measured by this technique is restricted, the upper limit being determined by the refractive index of the prism.

For several samples the refractive index in the draw direction exceeded that of the prism and hence could not be determined by the refractometer. This refractive index was therefore obtained indirectly by making observations of the birefringence in the plane of the film and combining this with the transverse index. The measurement was made by visually counting the number of interference fringes observed with polarized light between the unextended regions at the end of each sample and the drawn centre section. This number gives the birefringent path difference in wavelengths and corresponds to the product of the birefringence and the thickness.

For these samples the birefringent path difference varied between 7 and 19 wavelengths and could be determined most easily for the lowest draw ratio sample since this showed a more gradual transition from the high to the low draw regions. Since the fringe spacing varies with wavelength it is necessary to use a suitable monochromatic light source to observe the higher interference orders. In practice it was found to be convenient to observe the differences between samples by observing them in pairs with the draw direction of the first set perpendicular to that of the second and thus to determine the fringe displacement from the centre of one sample to the centre of the other of the zero order black fringe obtained with white light. Since essentially a material with the same basic optical properties is being used as a compensator this method avoids the so-called 'fringe jumping' experienced at high orders with standard

* To whom correspondence should be addressed

0032-3861/92/194207-03

Table 1 Variation of density, oxygen permeability coefficient and refractive indices with draw ratio for samples of PEEK

Sample number	Draw ratio	Density (ρ) ($g\,cm^{-3}$)	Refractive indices			Birefringence (n_1-n_2)	ρ_{calc}[a]	Oxygen permeability coefficient[b] ($\times 10^9$)
			n_1	n_2	n_3			
Isotropic	1.0	1.2650	1.681	1.681	1.677	0.000	–	8.3
8	1.6	1.2672	1.723	1.6715	1.657	0.0515	1.270	8.4
7	2.4	1.2744	1.773	1.6625	1.644	0.111	1.282	6.3
6	2.8	1.2805	1.792	1.6481	1.635	0.144	1.279	–
1	3.0	1.2840	1.800	1.6441	1.633	0.156	1.280	4.6
4	3.05	1.2850	1.818	1.6411	1.622	0.177	1.281	–
2	3.15	1.2845	1.812	1.6380	1.629	0.174	1.280	–
3	3.2	1.2842	1.827	1.6372	1.632	0.190	1.288	4.3

[a] Obtained from refractive index measurements
[b] Unit: $cm^3\,cm\,cm^{-2}\,cmHg^{-1}\,s^{-1}$

compensators where the wavelength dispersion of the birefringence in the compensator differs from that of the sample. Thickness measurements were made with an electronic digital micrometer and varied between 55 μm and 95 μm.

In order to confirm the consistency of the measurements, use can be made of the Lorentz–Lorentz relationship between the refractive indices and density given by:

$$\frac{3}{\rho_0}\left(\frac{n_0^2-1}{n_0^2+2}\right)=\frac{1}{\rho}\left[\frac{n_1^2-1}{n_1^2+2}+\frac{n_2^2-1}{n_2^2+2}+\frac{n_3^2-1}{n_3^2+2}\right] \quad (1)$$

where n_0 and ρ_0 are the refractive index and density of the isotropic material, respectively. Values calculated for ρ from this expression fall within 0.008 of the measured density values as shown in *Table 1*.

Oxygen permeability measurements

The oxygen diffusion properties were measured with an Oxtran permeability tester manufactured by Mocon Controls Inc. The method of operation followed previous studies on PET, where the instrument has been described in detail[5]. Essentially the sample to be measured provides a barrier between oxygen and nitrogen gas streams. Any oxygen which penetrates the barrier is collected by the nitrogen stream and detected by an oxygen sensor, the equilibrium response of which relates directly to the permeability.

RESULTS AND DISCUSSION

The oxygen permeabilities, together with density and refractive index values, are shown in *Table 1*. The refractive indices given by n_1, n_2 and n_3 correspond to the draw direction, the transverse direction in the plane of the sheet and the thickness direction, respectively. Although these results are not sufficiently comprehensive to allow a detailed analysis of the individual effects of crystallinity and orientation, it can be seen that the permeability of PEEK follows closely that observed for PET with only a small reduction when the draw ratio is increased. The refractive index measurements showed slight differences between the transverse and thickness directions indicating that the draw process is not completely uniaxial. The magnitude of the effect is however small and it is sufficient to consider the orientation to be represented by the birefringence in the plane of the surface. In *Figure 1* the permeability is

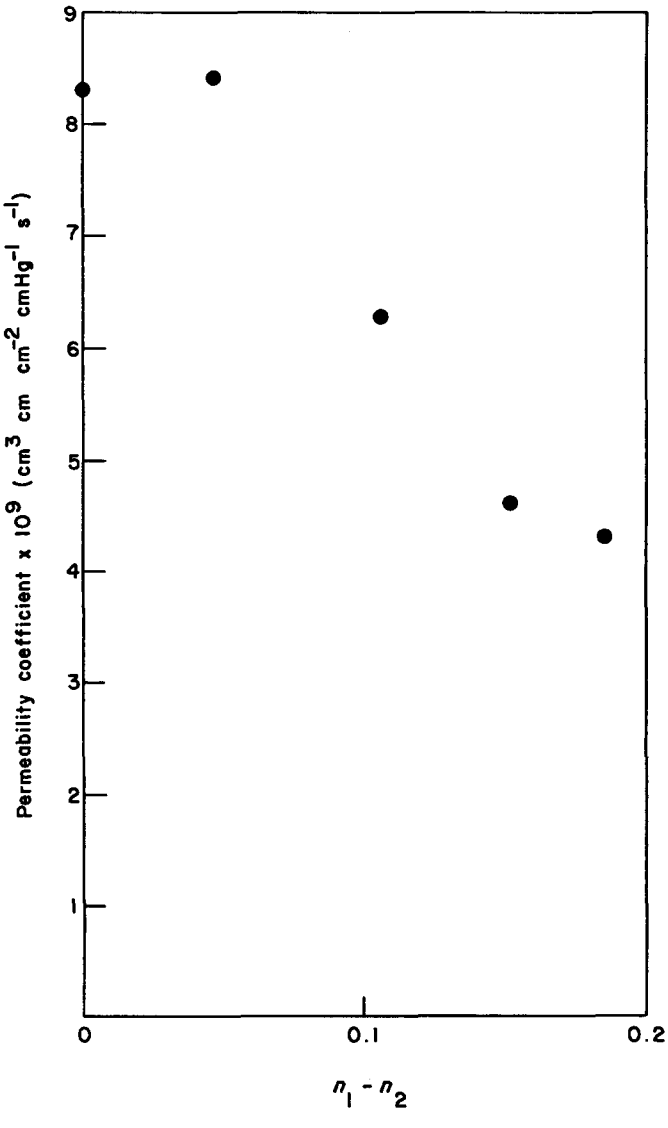

Figure 1 Variation of the oxygen permeability coefficient with birefringence

therefore plotted against the difference between the refractive indices in the draw direction and the transverse direction (n_1-n_2). After an initial small rise the permeability coefficient falls with increasing orientation and there is a reasonable correlation. The permeability falls by a factor of ~2 between the unoriented and the highly

Table 2 Impermeable fractions in PEEK

Sample number	Oxygen permeability coefficient[a] ($\times 10^9$)	Crystalline fraction[b] (f_c)	$\frac{2(1-f_c)}{2+f_c}$	$\frac{1-f_c}{1+f_c}$	Ideal f
Isotropic	8.3	0.0078	0.9883	0.9845	0
8	8.4	0.0250	0.9630	0.9512	–
7	6.3	0.0813	0.8829	0.8496	0.186
1	4.6	0.1563	0.7826	0.7297	0.358
3	4.3	0.1578	0.7806	0.7274	0.390

[a] Unit: $cm^3\,cm\,cm^{-2}\,cm\,Hg^{-1}\,s^{-1}$

[b] $f_c = \frac{\rho-\rho_a}{\rho_c-\rho_a}$ where $\rho_a = 1.264\,g\,cm^{-3}$ and $\rho_c = 1.392\,g\,cm^{-3}$

drawn material. This is very similar to results obtained previously for PET.

The crystallinity changes produced by drawing can be estimated from the density ρ. The crystalline fraction, f_c, is given by the equation:

$$f_c = \frac{\rho-\rho_a}{\rho_c-\rho_a} \quad (2)$$

where ρ_a and ρ_c are the densities of the amorphous and crystalline regions, respectively, which are assumed to be constant.

In PET it was shown that the permeability results could be satisfactorily understood on the basis of the Maxwell formula for the dispersion of impermeable spheres in a permeable matrix. The permeability P is then related to the impermeable fraction f by the proportionality:

$$P \propto \frac{2(1-f)}{2+f} \quad (3)$$

For PET it was shown that rather better agreement between the experimental data and equation (3) was obtained if f were the fraction of *trans* molecules rather than the crystalline fraction f_c.

In the case of PEEK, we have analysed the data on the basis of equation (3) assuming that f is given by f_c and the results are shown in *Table 2* and *Figure 2*. Following the work of Barrer and Petropoulas[6], and discussed by Petropoulas[7], we have also considered the case where the crystalline regions are envisaged to be long cylinders oriented at right angles to the direction of flow, which would give greater restriction to the permeability. In this case:

$$P \propto \frac{1-f}{1+f} \quad (4)$$

The corresponding calculated values for the PEEK samples are also shown in *Table 2* and *Figure 2*.

It can be seen from *Figure 2* that for both calculations the points fall below the line through the origin indicating that the change in the crystalline fraction, as determined from density measurements and based on ρ_a and ρ_c values, is too small to be solely responsible for the loss in permeability. The values required for the impermeable fraction to bring the points derived from equation (3) onto the line are shown in *Table 2* under the heading 'ideal f' and indicate that more than twice the number of impermeable elements are necessary. In the case of the highest draw ratio f would need to be 0.39, which corresponds to a density of $1.3140\,g\,cm^{-3}$. While this value is within the amorphous to crystalline density range it is well outside the error limit for the measured density

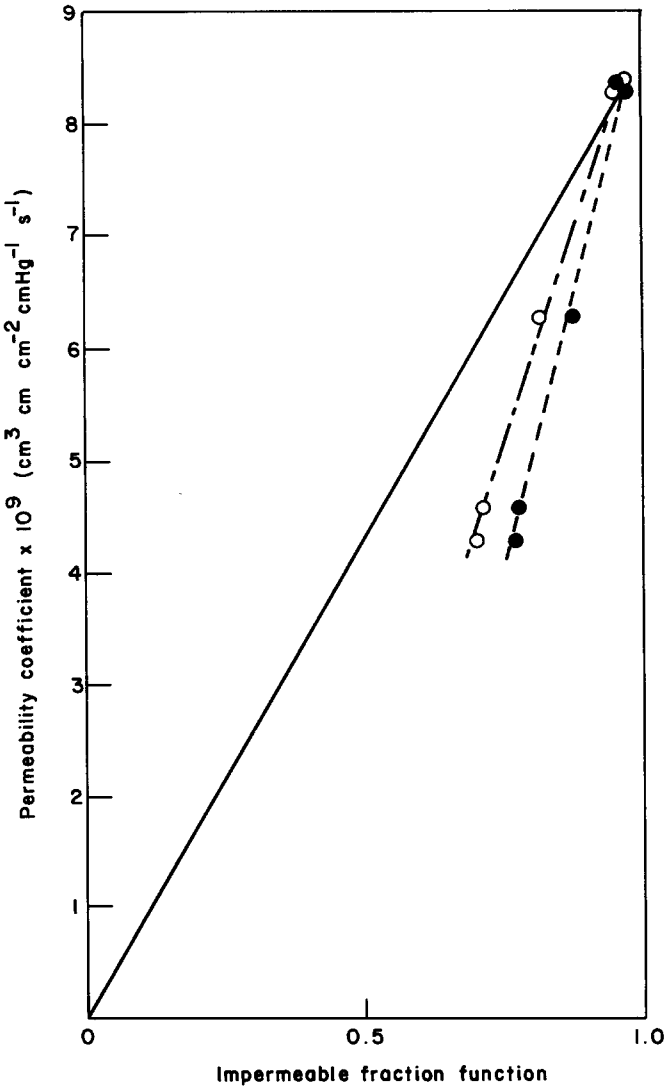

Figure 2 Effect of impermeable fraction on the oxygen permeability coefficient: (○) $2(1-f)/(2+f)$; (●) $(1-f)/(1+f)$

of $1.2842\,g\,cm^{-3}$. One possibility is that, as with PET, some parts of the amorphous component do not take part in the gas transmission. In addition, previous arguments are based on the assumption that the transmission of the permeable component remains constant as the crystalline volume fraction changes. The results suggest that this assumption may not be correct and that the increase in the orientation of the amorphous regions on drawing, may also be restricting the gas flow and hence contributing to the reduction in permeability. Both the birefringence and the difference between 'ideal f' and the observed f_c, i.e. the fractional part of the impervious amorphous component, increase with the draw ratio.

REFERENCES

1 Peterlin, A. *Pure Appl. Chem.* 1974, **39**, 239
2 Michaels, A. S. and Bixler, H. J. *J. Polym. Sci.* 1961, **50**, 393
3 Myers, A. W., Rogers, C. E., Stannett, V. and Szwarc, M. *Tappi* 1958, **41**, 716
4 Holden, P. S., Orchard, G. A. J. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 709
5 Slee, J. A., Orchard, G. A. J., Bower, D. I. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 71
6 Barrer, R. M. and Petropoulas, J. H. *Br. J. Appl. Phys.* 1961, **12**, 691
7 Petropoulas, J. H. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 1309