The Diffusion of Oxygen through Uniaxially and Biaxially Drawn Polypropylene

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Synopsis

The oxygen permeability of uniaxially and biaxially drawn polypropylene has been studied for both film and tube samples. With few exceptions the permeability coefficient decreases on drawing, but effects are small, particularly for biaxially drawn material where the coefficient does not fall below about 60% of the isotropic value. Molecular orientation as indicated by refractive index measurements appears as a major cause of the reduction in permeability.

INTRODUCTION

The transmission of gases through polymeric structures has been a subject for scientific investigation for many years. The barrier properties of polymer film have become very important in the food packaging and beverage bottling industry, where the low permeability polymers are in great demand. There are many approaches to changing the transport properties of polymer films and to decreasing penetrant permeability. The barrier properties of a material are partially dependent on its molecular characteristics, which can often be enhanced by orientation. In the commercial application of polymer films biaxial orientation is often used to improve the in-plane tensile strength and toughness. This also decreases the permeability. The effects of uniaxial orientation on permeability have been studied extensively,[1-4] but biaxially oriented polymer films lack a similar treatment despite their long-standing use in commercial applications.

Recent measurements of the diffusion of oxygen and helium through drawn films of polyethylene[2] have shown a very large fall in transmission compared with that of the isotropic material. This reduction is dependent on the draw ratio, and a significant drop occurs in the draw ratio range between 8 and 10. A new polymer tube die-drawing process has been developed in which the draw ratios obtained are typically in this region.[5] This process has been applied in one instance to obtain small-bore tubing from a polypropylene copolymer feedstock. For some applications where the exclusion of oxygen from the fluid passing through the tube is important, it is necessary to know what effect drawing has on the oxygen transmission of polypropylene. Since ultimately both uniaxial and biaxial drawing processes will be involved, some measurements have been made on currently available uniaxially and biaxially drawn tubes and others on uniaxially and biaxially drawn films.

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Preparation of Oriented Materials

Films

Films were prepared from both homopolymer and copolymer grades of polypropylene. The homopolymer was Diamond Shamrock S100 grade (M_w = 200,000, mp 154.5°C). The copolymers were ICI plc grades GSE 108 (MFI 0.8, M_w = 542,000, mp 161.5°C) and GPE 102 (MFI 0.3, M_w = 540,000, mp 161.5°C). Isotropic sheets of the S100 and GSE 108 polymers approximately 1.0 mm thick were prepared by compression molding at 210°C and quenching into cold water. For the GPE 102 copolymer the feedstock was obtained in the form of commercially available sheets of Propylex D9550, 1.5 mm thick. With the S100 polymer dumbbell samples of gauge length 18 × 72 mm wide were cut from the prepared sheets and were drawn in air on an Instron Tensile Testing machine at a crosshead speed of 100 mm/min and a draw temperature of 115°C. Draw ratios of about 8 and 12.5 were obtained as determined from the displacement of ink lines drawn perpendicular to the draw direction on the surface of the undrawn material. The GPE 102 copolymer was similarly drawn but with a gauge length 15 × 100 mm wide, a crosshead speed of 50 mm/min, and a draw temperature of 135°C. A series of samples with different draw ratios ranging from 7.2 to 15 was prepared.

Both copolymers were also biaxially drawn. This was done on a Bruckner two-way stretch machine that allows simultaneous or sequential drawing along two perpendicular directions in a hot air oven. A wide range of samples was produced at a draw temperature of 150°C. These samples were produced either by simultaneously drawing to similar draw ratios along two perpendicular directions in the plane of the sheet or by initially drawing along one direction at constant width and then subsequently drawing along the perpendicular direction to various draw ratios to obtain an unbalanced structure. Subsequently a limited number of samples were drawn uniaxially on the Bruckner machine at temperatures ranging between 115 and 155°C.

The Bruckner machine requires a minimum sample dimension along the direction of draw of 23 cm, and the draw speed was 60 cm/min, which corresponds to a strain rate of about 300% per minute. No attempt has been made to examine the effect of strain rate on the results.

The uniaxial drawing process introduces some lateral shrinkage and, nominally, at constant volume, the magnitude will be given by the reciprocal of the square root of the draw ratio. For wide sheets the retraction in the plane of the sheet is restricted, and slight departures from uniaxial drawing may occur. The figures shown in brackets in Table I for the Bruckner-drawn samples indicate the draw ratios obtained for the transverse direction in the plane of the sheet.

Tubes

The tubes were produced by die drawing a tubular billet of the appropriate polypropylene copolymer grade supplied by ICI plc. A full account of the method is published elsewhere,[5] but briefly the billet is drawn through a heated circular die and over a cylindrical mandrel at various draw speeds to obtain different draw ratios. For linearly drawn tubes a draw temperature of 110°C was used, and the draw ratio was determined from the ratio of the cross-sectional areas

TABLE I
Oxygen Permeability Coefficients Obtained with Uniaxially Drawn Polypropylene Films

Polymer grade	Draw temp. (°C)	Drawing method	Draw ratio	Thickness (μm)	Permeability coeff. $\times 10^{11}$ [cm^3cm/cm^2/ (cm Hg)s]
S100 homopolymer			Isotropic	336	10.3
S100 homopolymer	115	Instron	8	66	3.58
S100 homopolymer	115	Instron	12.5	77	2.82
Propylex D9550 (GPE 102 copolymer)			Isotropic	125	15.6
Propylex D9550 (GPE 102 copolymer)	150	Bruckner	6.8	335	9.64
Propylex D9550 (GPE 102 copolymer)	115	Bruckner	8.7 ($\times$ 0.36)	490	5.91
Propylex D9550 (GPE 102 copolymer)	125	Bruckner	8.7 ($\times$ 0.40)	445	7.10
Propylex D9550 (GPE 102 copolymer)	130	Bruckner	8.5 ($\times$ 0.42)	435	6.62
Propylex D9550 (GPE 102 copolymer)	135	Bruckner	8.7 ($\times$ 0.44)	410	6.49
Propylex D9550 (GPE 102 copolymer)	140	Bruckner	8.3 ($\times$ 0.45)	415	7.80
Propylex D9550 (GPE 102 copolymer)	145	Bruckner	8.3 ($\times$ 0.47)	411	8.89
Propylex D9550 (GPE 102 copolymer)	155	Bruckner	8.4 ($\times$ 0.55)	345	10.3
Propylex D9550 (GPE 102 copolymer)	135	Instron	7.2	242	11.07
Propylex D9550 (GPE 102 copolymer)	135	Instron	8.2	220	10.03
Propylex D9550 (GPE 102 copolymer)	135	Instron	9.6	200	8.14
Propylex D9550 (GPE 102 copolymer)	135	Instron	13.0	170	4.43
Propylex D9550 (GPE 102 copolymer)	135	Instron	15.0	160	3.55

before and after drawing. These tubes were produced from the GPE 102 grade polymer with a wall thickness of about 800 μm. Two samples with linear draw ratios of 9 and 10, respectively, were selected for oxygen diffusion measurements. A third tube from GSE 108 polymer was biaxially drawn at 153°C and was sufficiently thin to be cut lengthwise and opened out to provide a flat film sample.

Diffusion Measurements

The diffusion measurements were made by a continuous flow technique with the Oxtran 100 permeability equipment (manufacturers Modern Controls Inc.). In this method a continuous flow of gas is maintained on both sides of the barrier material. Initially nitrogen gas is passed over both surfaces to remove oxygen in the sample. The nitrogen on one side is then replaced by oxygen,

and the nitrogen flow on the other side then sweeps the surface to extract any oxygen that diffuses through the material. The diffusing oxygen is measured by a detector that is sensitive only to oxygen. Further details are given in Ref. 2.

The same equipment has been used to make measurements on both drawn films and on drawn tubes. The Oxtran 100 equipment has two measuring positions, one of which is designed to examine the material in sheet form with an exposed circular area of 100 cm^2 while the other can be adapted to take auxiliary cells. Since the large area could not be obtained from the samples available, both the film and the tubes were measured with auxiliary units. The film areas measured were about 5 cm^2, and the tube areas in the region 90–130 cm^2 depending on the diameter and exposed length. The cells are shown schematically in Figure 1.

Density

Densities were measured at room temperature in a conventional density gradient column using the liquids diethylene glycol (digol) and propan-2-ol.

Measurement of Refractive Indices

Refractive indices n_M, n_T, and n_N along the three mutually perpendicular machine / 1st draw, transverse / 2nd draw, and film normal directions were measured by an Abbe refractometer equipped with a polarizing eyepiece. A Cargille refractive index liquid with $n_D = 1.5400$ was used as an immersion liquid.

RESULTS

The results obtained with films are shown in Tables I and II for the uniaxially drawn and biaxially drawn samples, respectively. Table III shows the results
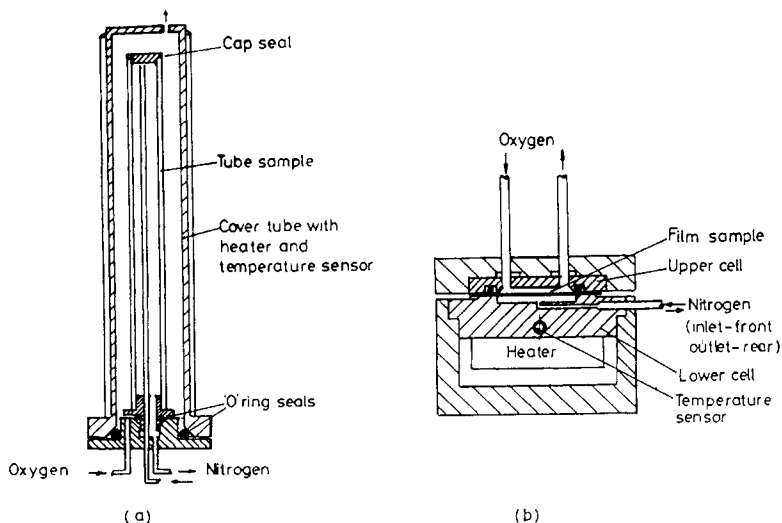

Fig. 1. Schematic diagram of Oxtran attachments to measure (a) polymer tubes and (b) small area films.

TABLE II
Oxygen Permeability Coefficient Obtained with Biaxially Drawn Polypropylene Films

Polymer grade	Draw temp. (°C)	Draw ratio	Thickness (μm)	Permeability coeff. $\times 10^{11}$ [cm^{3}cm/cm^2/(cm Hg)s]
Propylex D9550 (GPE 102 Copolymer)		Isotropic	125	15.6
Propylex D9550 (GPE 102 Copolymer)	150	3 $\times$ 3	150	12.6
Propylex D9550 (GPE 102 Copolymer)	150	5 $\times$ 5	60	11.7
Propylex D9550 (GPE 102 Copolymer)	150	6 $\times$ 6	49	10.9
Propylex D9550 (GPE 102 Copolymer)	150	8 $\times$ 8	23	9.32
Propylex D9550 (GPE 102 Copolymer)	150	6.7 $\times$ 0.85[a]	275	11.2
Propylex D9550 (GPE 102 Copolymer)	150	6.5 $\times$ 1.05[a]	235	13.0
Propylex D9550 (GPE 102 Copolymer)	150	6.5 $\times$ 1.6[b]	150	12.9
Propylex D9550 (GPE 102 Copolymer)	150	6.8 $\times$ 4.0[b]	54	10.8
Propylex D9550 (GPE 102 Copolymer)	150	6.5 $\times$ 6.0[b]	39	10.1
Propylex D9550 (GPE 102 Copolymer)	155	8.2 $\times$ 0.7[a]	258	11.4
Propylex D9550 (GPE 102 Copolymer)	155	8.2 $\times$ 1.25[b]	150	11.2
Propylex D9550 (GPE 102 Copolymer)	155	8.3 $\times$ 4.0[b]	45.6	10.6
Propylex D9550 (GPE 102 Copolymer)	155	8.2 $\times$ 5.7[b]	32.3	10.1
Propylex D9550 (GPE 102 Copolymer)	155	8 $\times$ 7[b]	26.5	10.1
GSE 108 Copolymer		Isotropic	505	14.0
GSE 108 Copolymer	150	4.7 $\times$ 4.9	49.3	11.0
GSE 108 Copolymer	150	6 $\times$ 7	27.8	10.5
GSE 108 Copolymer	150	6.9 $\times$ 6.9	23.0	9.42
GSE 108 Copolymer	150	7.8 $\times$ 7.9	14.6	9.53

[a] Restricted widthwise retraction.
[b] Sequentially drawn.

obtained with tubes. There is some indication from Table I that copolymer samples prepared on the Bruckner machine give lower permeability coefficients than those of samples drawn on the Instron machine at similar draw ratios and at nominally the same temperature. These two machines operate on different sample sizes (200 mm between clamps, cf. 18 mm) and at different draw speeds, and hence some structural differences may occur due to transverse contraction. In order to avoid possible spurious conclusions introduced by these differences, comparisons will be restricted to the separate Instron or Bruckner results. Figure 2 shows the variation in the permeability coefficient with draw ratio for the film samples uniaxially drawn on the Instron. Both the homopoly-

TABLE III
Oxygen Permeability Coefficient Obtained with Biaxially Drawn Polypropylene Tubes

Polymer grade	Draw temp. (°C)	Draw ratio	Thickness (μm)	Permeability coeff. $\times 10^{11}$ [cm^{3}cm/cm^2/(cm Hg)s]
GSE 108 copolymer biaxially drawn tube	153	6.2 $\times$ 2.8	222	7.94
GPE 102 copolymer tube feedstock		Isotropic	750[a]	10
Linearly drawn tube	110	9	830	3.25
Linearly drawn tube	110	10	775	3.34

[a] Difficulties in the preparation of a suitable tube of isotropic material from the thick-walled feedstock resulted in a variable wall thickness and hence only approximate figures are available.

mer and the copolymer show a fall in permeability on drawing. The reduction is greatest for the homopolymer drawn at 115°C. The effect of draw temperature can be seen in Figure 3 for measurements made on copolymer samples drawn on the Bruckner machine. These show a progressive drop in the permeability as the draw temperature is reduced, although at the two lowest temperatures, where voiding was observed in the drawn material, there is a discontinuity in the trend.

The results on the biaxially drawn films shown in Table II again indicated a reduction in permeability on drawing, but, in spite of the large differences in
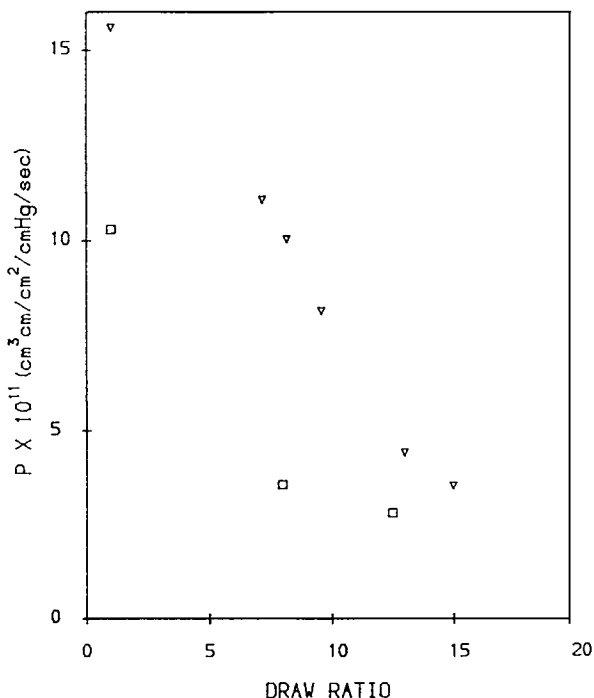

Fig. 2. The effect of draw ratio on the oxygen permeability of uniaxially drawn homopolymer and copolymer films: □ S100 homopolymer T_d 115°C, ∇ GPE 102 copolymer T_d 135°C.
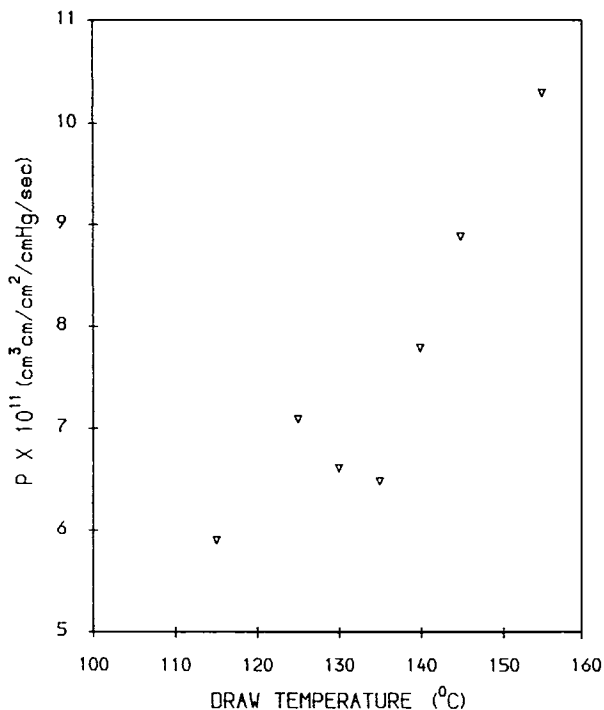
Fig. 3.   The effect of draw temperature on the oxygen permeability of uniaxially drawn films of GPE102 polypropylene copolymer at a draw ratio of about 8.5.

area expansion between the various drawn samples, the permeability coefficient does not vary greatly between them. Figure 4 shows the relationship between the permeability coefficient and the surface area expansion for the simultaneously biaxially drawn samples. In the case of sequentially biaxially drawn samples, the permeability coefficient increases initially as the samples were drawn in the transverse direction to very low draw ratios. On further drawing to higher draw ratios in the transverse direction, the permeability coefficient decreases. This is shown in Figure 5. The greatest permeability reduction for both simultaneously and sequentially biaxially drawn sheets is obtained at the highest draw, but even then the permeability coefficient does not fall below about 60% of the isotropic value.

The tubes were drawn at two temperatures as shown in Table III. The uniaxially drawn tubes of GPE 102 copolymers drawn at 110°C show a similar permeability drop to that of the uniaxially drawn film samples produced at low draw temperature. The biaxially drawn sample of GSE 108 copolymer drawn at higher temperature does not show such a large fall in permeability but behaves similarly to the films drawn biaxially at a similar temperature.

DISCUSSION

Earlier measurements made on polyethylene films showed a reduction in the oxygen permeability coefficient by a factor of about 5 by draw ratio 10, when
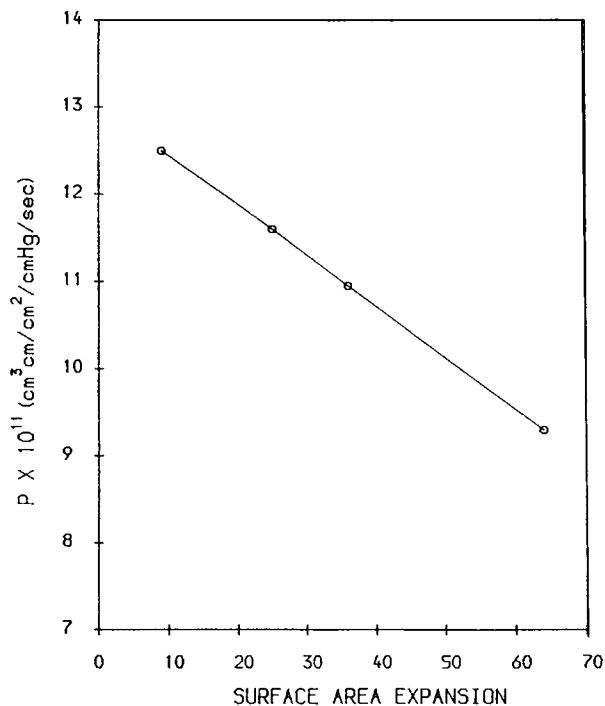
Fig. 4.　The effect of surface area expansion on the oxygen permeability of simultaneously biaxially drawn films of GPE102 polypropylene copolymer.

orientation is complete, and a further drop, up to ten times in some cases, for higher draw ratios. For polypropylene the results show that, although the drawing process, whether uniaxial or biaxial, always reduces the permeability, the reduction obtained is not as great as that found with polyethylene.

Biaxial drawing does not show very much variation in the permeability coefficient over a wide range of draw ratios, and the largest changes are obtained for the uniaxially drawn samples when the draw temperature is reduced.

The gaseous diffusion process has been found previously to take place in the amorphous regions of polymers. We would therefore consequently expect a reduction in the permeability as the crystallinity rises. For polyethylene, as the polymer is drawn, there is a small increase in crystallinity, as shown by density measurements, but this makes only a small contribution to the large permeability change, which is dominated by structural orientation effects. Density measurements obtained from various polypropylene samples are given in Table IV. These show that the density and hence the crystallinity decrease as the draw temperature is reduced. The resulting fall in the permeability cannot therefore be attributed to a decrease in the amorphous content but must be attributed to structural changes, most probably orientation of the amorphous regions. This is supported by the modulus results obtained on the same uniaxially drawn samples where there is an excellent inverse correlation between modulus and permeability, and the modulus is highest for the lowest draw temperature sample with the lowest permeability coefficient in spite of some stress whitening. These results are shown in Figure 6. There is also indirect
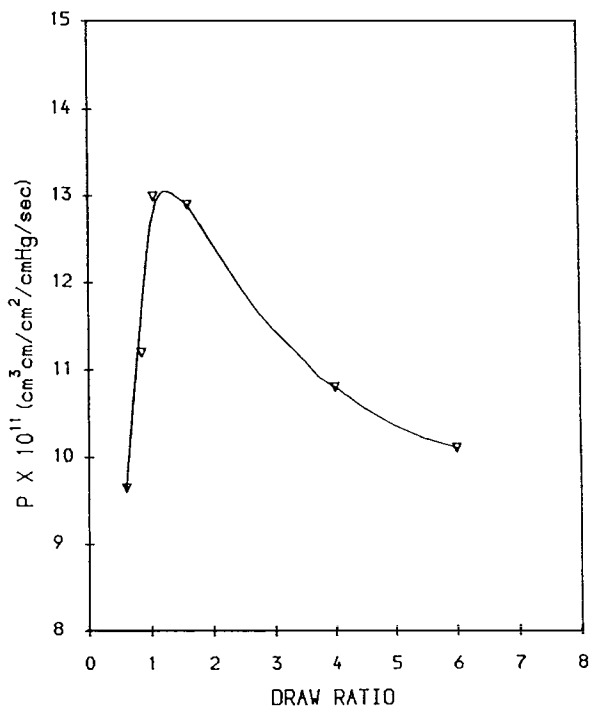
Fig. 5. The effect of draw ratio in the transverse direction on the oxygen permeability of sequentially biaxially drawn films of GPE102 polypropylene copolymer. Draw ratio in the machine direction is about 6.5.

support for this hypothesis from the density values obtained with the biaxially drawn samples where both the crystallinity and the permeability fall with increasing draw ratio.

It is proposed therefore that molecular orientation is the primary factor that affects the passage of the gas molecules and hence the barrier properties. The optical anisotropy is shown by the dependence of the refractive index on the plane of polarization, and the results given in Table V show that the highest index mostly occurs in the machine direction. For uniaxially drawn materials the extent of the orientation can be determined from the birefringence since perfect alignment of the structural units along the draw direction will give rise to a maximum birefringence value, and the extent to which this is achieved can be expressed as an orientation factor, f, related to the mean orientation by

$$ f = \frac{\Delta n}{\Delta n_{\max}} = \left\langle \tfrac{1}{2}(3 \cos^2\theta - 1) \right\rangle $$

where θ is the angle between the major axis in the structural unit and the draw direction.

For biaxially drawn materials, in which the three refractive indices differ, the birefringence has sometimes been expressed as a value normal to the film. In this usage an average has been taken of the indices in the plane of the film

TABLE IV
Variation of Density and Modulus with Draw Conditions for Propylex D9550 Films

Draw temp. (°C)	Draw ratio	Density (g/cm^3)	% Crystalline[a] volume fraction	Longitudinal modulus (GPa)
115	8.7 (× 0.36)	0.8965	52.4	6.1
125	8.7 (× 0.40)	0.8990	55.4	5.7
130	8.5 (× 0.42)	0.9010	57.8	5.4
135	8.7 (× 0.44)	0.9015	58.4	5.9
140	8.3 (× 0.45)	0.9030	60.2	4.4
145	8.3 (× 0.47)	0.9037	61.1	3.75
155	8.4 (× 0.55)	0.9043	61.8	3.75
—	Isotropic	0.8915	46.4	1.15
150	3 × 3	0.9015	58.4	1.55
150	5 × 5	0.9000	56.6	3.05
150	6 × 6	0.8975	53.6	3.85
150	8 × 8	0.8960	51.8	4.2

[a] Calculated from $(d - d_a)/(d_c - d_a)$ with $d_c = 0.936$, $d_a = 0.853$.[6]

and the difference between this and the refractive index in the thickness direction has been adopted as a birefringence. The birefringence Δn_N is then given by
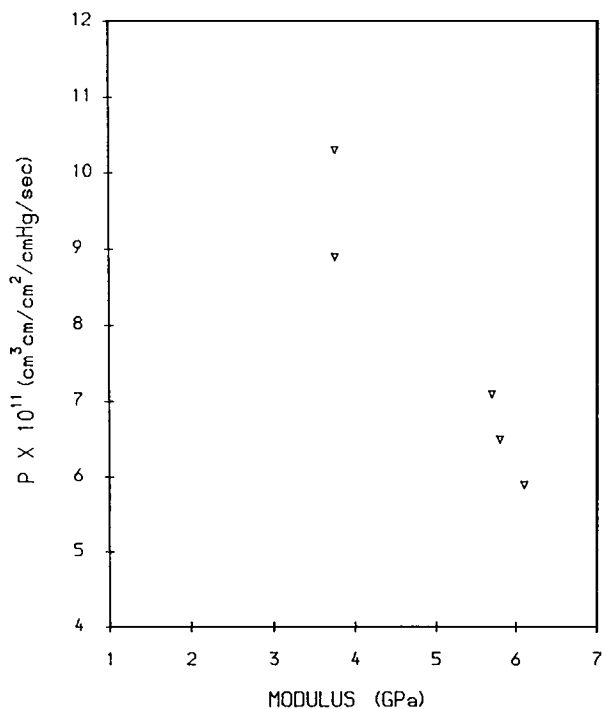

Fig. 6. The correlation between modulus and oxygen permeability of uniaxially drawn films of GPE102 polypropylene copolymer drawn at different temperatures to a constant draw ratio of about 8.5.

TABLE V
Variation of Oxygen Permeability with Refractive Indices for Drawn Polypropylene Films

Sample	n_M	n_T	n_N	Δn_N $(\times 10^3)$	Δn_{total} $(\times 10^3)$	$P \times 10^{11}$ [cm^{3}cm/cm^2/ (cm Hg)s]
S100 homopolymer						
Uniaxial $\lambda = 12.5/13$	1.5285	1.4931	1.4931	17.7	35.4	2.82
$\lambda = 8$	1.5264	1.4940	1.4940	16.2	32.4	3.58
GPE 102 copolymer						
Uniaxial $\lambda = 15$	1.5265	1.4940	1.4940	16.25	31.5	3.6
$\lambda = 9.6$	1.5229	1.4954	1.4954	13.75	27.5	8.14
$\lambda = 7.2$	1.5204	1.4958	1.4958	12.3	24.6	11.1
Simultaneously biaxially drawn						
3×3	1.5042	1.5073	1.4994	6.35	6.9	12.6
5×5	1.5073	1.5073	1.4958	11.50	11.5	11.7
6×6	1.5082	1.5069	1.4949	12.65	12.7	10.9
8×8	1.5082	1.5035	1.4931	12.75	13.4	9.32
Seq. drawn						
6.8×0.85	1.5208	1.4980	1.4976	11.8	23.0	11.2
6.5×1.05	1.5195	1.4994	1.5002	9.25	19.7	13.0
6.5×1.6	1.5178	1.5002	1.4994	9.6	18.0	12.9
6.5×6.0	1.5056	1.5082	1.4958	11.1	11.3	10.1
GSE 108 copolymer simultaneously biaxially drawn						
4.7×4.9	1.5055	1.5055	1.4949	10.6	10.6	11.0
6×7	1.5082	1.5047	1.4945	11.95	12.33	10.5
6.9×6.9	1.5104	1.5047	1.4958	11.75	12.75	9.42
7.8×7.9	1.5073	1.5073	1.4931	14.2	14.2	9.53

$$\Delta n_N = \tfrac{1}{2}(n_M + n_T) - n_N = \tfrac{1}{2}(n_M - n_N) + \tfrac{1}{2}(n_T - n_N)$$

Where n_M and n_T are equal, this will be equivalent to the uniaxial case, but with the film normal direction replacing the machine direction as the reference axis. If, however, this equation is applied to a uniaxial sample, in which n_T and n_N are equal, the resulting "birefringence" will be only a half of the conventional value.

An alternative expression that considers the total birefringence from the three mutually perpendicular planes by taking the indices in pairs is given by Δn_{total} where

$$(\Delta n_{\text{total}})^2 = \tfrac{1}{2}(n_M - n_T)^2 + \tfrac{1}{2}(n_T - n_N)^2 + \tfrac{1}{2}(n_N - n_M)^2$$

Δn_{total} will be equal to Δn_N when n_M and n_T are equal and will give the conventional value for uniaxial samples $(n_T = n_N)$. The difference between the two expressions lies mainly in the inclusion of the difference between the sample surface indices in the second case.

The two Δn functions are plotted against the permeability coefficient in Figure 7(a) and (b). Figure 7(a) shows that, in general, the permeability falls
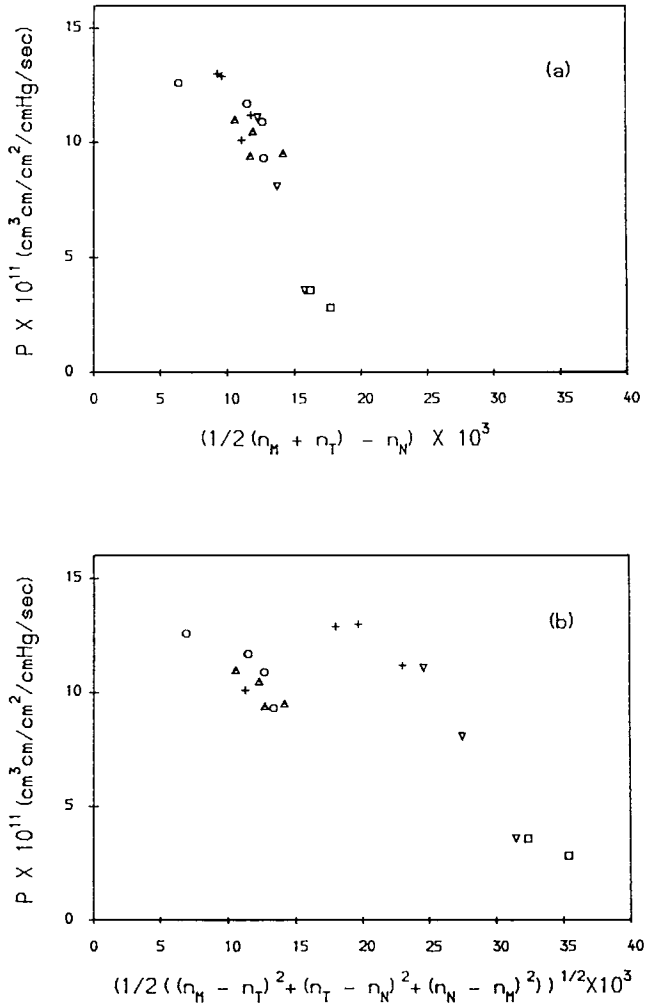
Fig. 7. The effect of the refractive index differences on the oxygen permeability of uniaxially and simultaneously and sequentially biaxially drawn films of GPE102 polypropylene copolymer. (a) Values referred to the refractive index normal to the surface and (b) total birefringence results. Uniaxially drawn: $\square$ S100, ∇ GPE 102; simultaneously biaxially drawn: $\triangle$ GSE 108, $\bigcirc$ GPE 102; sequentially biaxially drawn: $+$ GPE 102.

as Δn_N increases with both uniaxial and biaxial samples following a similar pattern. In Figure 7(b) the uniaxial samples and those biaxially drawn sequentially with a low transverse draw ratio show higher Δn_{total} values and hence form a separate group. The two groups each show a fall in permeability as Δn_{total} increases. Taken together the results suggest that orientation in the plane of the sheet plays a less significant part in determining the permeability coefficient for gas flow through it. It is nevertheless necessary to draw uniaxially to obtain any appreciable drop in the permeability level. Figure 7 confirms that the permeability decreases with increasing orientation in the sample but suggests that there is a degree of complexity that requires further detailed structural studies.

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