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Effect of annealing on the permeation characteristics of gases of coextruded LLDPE films

Vicente Compañ, Andreu Andrio and María L. López
Departamento de Física, Universitat Jaume I, 12080 Castellón, Spain

and Evaristo Riande*
Instituto de Ciencia y Tecnología de Polímeros, CSIC, 28006 Madrid, Spain
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The temperature dependence of both the permeability and diffusion coefficients of carbon dioxide, oxygen and nitrogen in annealed LLDPE films are studied. It is found that the values of the permeability coefficient through the annealed membranes are nearly four times larger than those through the non-annealed ones. The fact that annealing slightly diminishes the values of the diffusion coefficient leads to the conclusion that the rise in permeability detected in the films by effect of annealing should be attributed to an increase in solubility. The permeability characteristics of the films are interpreted in terms of the free volume theory. Copyright © 1996, Elsevier Science Ltd.

INTRODUCTION

Extensive work carried out by Michaels and coworkers[1,2] and others[3] suggested that gas transport in polyethylene films occurs nearly exclusively through the noncrystalline phase, so that the crystalline regions only act as physical barriers to impede the flow. The effect of orientation on permeation was studied on ultrahigh modulus polyethylene films prepared by tensile drawing of polyethylene in the solid phase[4]. In this case the barriers impeding the flow and their effect on the packing density in the crystalline–amorphous interfaces depend on both the molecular orientation and the size of the permeant molecules. A thorough study dealing with the permeation and diffusive aspects of these films was carried out by Holden et al.[5] showing that the solubility of the gas in the oriented film is proportional to the amorphous volume fraction as occurs in undrawn films. However, a significant decrease in the diffusion coefficient with increasing draw ratio was observed, which is particularly important in the case of larger size permeant molecules.

Coextruded linear low density polyethylene (LLDPE) films, like highly oriented polyethylene, exhibit good ultimate properties which confers them important applications in the packaging of foodstuffs. The combination of a relatively low crystallinity and a moderate orientation, which are mainly responsible for the good ultimate mechanical properties of these films[6], may affect the permeation of gases through them. The physical barriers to gas permeation provided by the crystalline entities and their influence on the packing density in the relatively ordered crystalline–amorphous interfaces will depend on the molecular orientation of the films. The microstructure of the films is governed by the chemical composition of the linear low density raw materials and the processing conditions, mainly speed extruders, distance between die and chill roll, vacuum knife depression, distance between die and frost line and line speed. Earlier studies carried out on the permeation of coextruded LLDPE films did not show a noticeable dependence on the processing conditions. Thus, the analysis of the temperature dependence of the permeability coefficient, P, of carbon dioxide through these films showed in all cases a significant increase in the values of P between 27 and 52°C, followed by a small plateau in which the permeability coefficient remains nearly constant. The permeability coefficient of oxygen followed similar trends, although the changes of this parameter with temperature were less ostensible.

The differential scanning calorimetry (d.s.c.) thermograms of the coextruded LLDPE films present a single peak associated with the melting of the crystalline phase whose departure from the baseline and maximum are located, respectively, at 60 and 120°C[7]. The peak's breadth suggests a wide distribution of crystalline size entities and for this reason it was felt interesting to investigate how annealing of the films would affect their permeation characteristics. Consequently, this work describes a comparative study of the temperature dependence of both the permeability and the diffusion coefficients of carbon dioxide, oxygen and nitrogen through two annealed films obtained using different processing conditions and the results are interpreted by means of the free volume theory.

* To whom correspondence should be addressed

EXPERIMENTAL

The films were prepared by Manuli Stretch S.P.A. (Italy)[6]. The raw materials used in the preparation of the films were copolymers of ethylene-*co*-octene (Dow-Chemical, Tarragona, Spain) with a content of *ca* 8 mol% of the latter comonomer. The two films used in this study were made up of three layers CAB where the first and the second layers (C and A) are Dowlex 2247 ($\rho = 0.917\,\mathrm{g\,cm^{-3}}$) whereas the third layer (B) is Dowlex 2291 ($\rho = 0.912\,\mathrm{g\,cm^{-3}}$). The thickness of the first, second and third layers were 3.5, 16 and 3.5 μm respectively. The films that will be called LLDPE7 and LLDPE12 were obtained using the same raw materials but slightly different processing conditions. Thus the distances between die and chill roll were 15 and 5 mm, respectively, for LLDPE12 and LLDPE7; another difference in the processing conditions was that the vacuum knife depression for LLDE7 and LLDPE12 films amounted to 2.05 and 5 cm Hg, respectively. The rest of the processing conditions, which include speeds of extruders C, A and B, line speed and distance between die exit and frost line, were the same.

Important differences were not observed in the ultimate properties (ultimate elongation, yield stress, ultimate stress, energy break and load at break) corresponding to both films. The degree of crystallinity as determined from the melting endotherms was 0.30 in both cases and the birefringence Δn amounted to 3.6×10^{-3} and 2.6×10^{-3} for LLDPE7 and LLDPE12, respectively[6]. The films to be used in the permeation measurements were annealed at 80°C for 2 h and the values of $10^3 \Delta n$ for the former and latter films decreased to 2.4 and 1.8, respectively.

Measurements of the permeability of oxygen, carbon dioxide and nitrogen were performed using an experimental set up in which two chambers coupled to pressure sensors are separated by the film whose permeation is to be measured. The experimental device together with the gas reservoir were placed inside a thermostat, and before allowing the gas to flow from the reservoir to the high pressure chamber a vacuum was applied throughout all the experimental setup. Then by keeping the pressure at 155.0 ± 1 mm Hg ((0.1759 ± 0.0133)Pa) in the high pressure chamber, the gas flowing through the membrane to the low pressure chamber was monitored by measuring the pressure as a function of time. The permeation measurements were made from 298 to 353 K. More details about the permeation measurements are given elsewhere[7].

RESULTS AND DISCUSSION

The transport of gases through membranes is generally expressed in terms of the permeability coefficient, P, and the diffusion coefficient, D, where this last term can be obtained from Fick's second law. Once steady state conditions are reached, the amount of gas diffusing at time t is given by[8,9]

$$Q(t) = \frac{DC_0}{l}\left(t - \frac{l^2}{6D}\right) \tag{1}$$

where C_0 is the gas concentration in the high pressure chamber and l is the film thickness. The permeability coefficient can be evaluated from $\mathrm{d}Q/\mathrm{d}t$ by using the following relationship[7]

$$P = \frac{273}{76}\left(\frac{Vl}{ATp_0}\right)\left(\frac{\mathrm{d}p(t)}{\mathrm{d}t}\right) \tag{2}$$

where V is the volume of the low pressure chamber, A is the effective film area, p_0 is the pressure in cm of Hg of penetrant gases in the high pressure chamber, $\mathrm{d}p(t)/\mathrm{d}t$ is the rate of pressure measured by the pressure sensor in the low pressure chamber and T is the absolute temperature of the thermostat. The unit used to express the permeability coefficient is the barrer ($= 10^{-10}\,\mathrm{cm^3}$ (STP) $\mathrm{cm/cm^2\,s\,cm}$ of $\mathrm{Hg^{-1}}$). The diffusion coefficient can be obtained from $Q(t)$ by the lag method suggested by Barrer[10]

$$D = \frac{l^2}{6\theta} \tag{3}$$

where θ, the time lag, can be determined from the intercept of $Q(t)$ on the time axis.

Since the determination of the diffusion coefficient involves the use of the square of the thickness of the films, small errors in the value of l may give rise to uncertainties in the value of the diffusion coefficient which are larger the smaller is l. Uncertainties in D can also derive from the lag method in the sense that the smaller is l, the lower is θ and, consequently, the larger is the error involved in the determination of the time lag. In order to avoid these difficulties, the permeation measurements were carried out on membranes made up of three films which were firmly stuck together with a rolling cylinder at room temperature. Boundary effects at the interface between films were not detected, as indicates the fact that the values obtained for the permeability coefficients are similar in the thermally untreated laminate membranes and in the corresponding films.

Values of the permeability coefficient CO_2 through the LLDPE12 membrane are represented as a function of temperature in *Figure 1*. It should be noted that the filled symbols represent experimental values of P determined from low to high temperature whereas the unfilled ones correspond to measurements carried out from high to
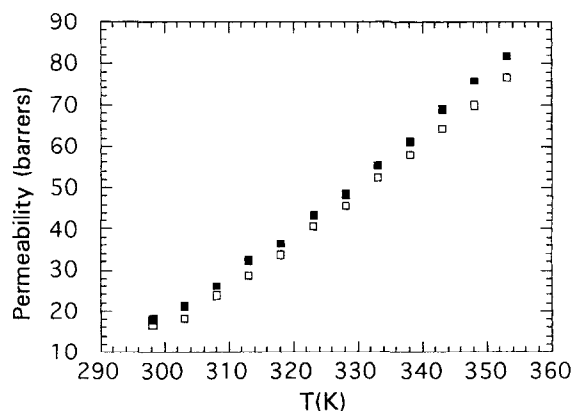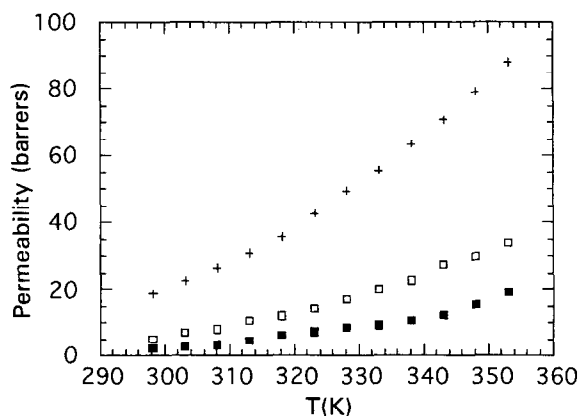

Figure 1 Values of the permeability coefficient of CO_2 as a function of temperature for annealed LLDPE12 films. Filled symbols represent results obtained from low to higher temperatures whereas the unfilled ones were obtained in reverse temperature order
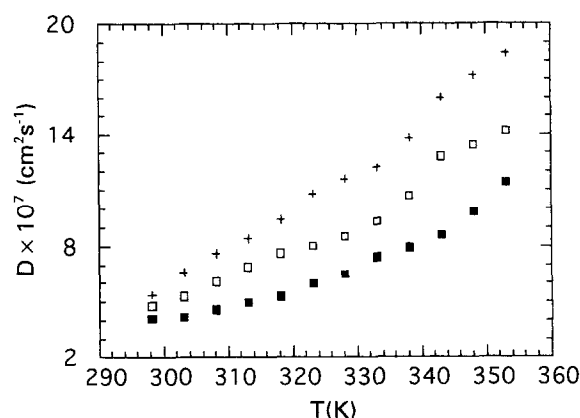
Table 1 Effect of annealing on the permeability coefficient in barrers and the diffusion coefficient in $10^{-7}\,cm^2\,s^{-1}$ for N_2, O_2 and CO_2 through LLDPE7 and LLDPE12 films

T (°C)	Non-annealed sample						Annealed sample					
	$P(N_2)$	$P(O_2)$	$P(CO_2)$	$D(N_2)$	$D(O_2)$	$D(CO_2)$	$P(N_2)$	$P(O_2)$	$P(CO_2)$	$D(N_2)$	$D(O_2)$	$D(CO_2)$
LLDPE7 Film												
25	0.75	1.2	12.2	1.6	2.3	3.2	0.87	4.5	17.2	1.4	2.0	2.5
50	3.6	10.4	30.5	2.6	4.2	6.0	4.5	15.9	41.9	2.4	3.8	5.3
LLDPE12 Film												
25	0.90	2.1	13.5	4.3	5.1	5.6	2.2	5.1	18.6	4.1	4.8	5.4
50	4.1	11.2	34.7	6.4	8.4	11.2	7.2	14.2	42.6	6.0	8.0	10.8

Figure 2 Temperature dependence of the permeability coefficients of CO_2 (+), O_2 (□) and N_2 (■) through annealed LLDPE12 films

Figure 3 Variation with temperature of the diffusion coefficients of CO_2 (+), O_2 (□) and N_2 (■) through annealed LLDPE12 films

low temperatures. The results obtained from measurements carried out in decreasing temperature order are consistently slightly lower than those obtained in reverse order, suggesting that small changes take place in the microstructure of the film presumably connected with crystallites thickening occurring at high temperatures. A similar hysteresis process is also observed in the permeation measurements performed on LLDPE7 membranes.

As usual[11], the permeability coefficient of carbon dioxide is much larger than that of oxygen and nitrogen, as can be seen in *Figure 2* where, for illustrative purposes, the permeabilities of the three gases used in this study through LLDPE12 membranes are shown. It is worthy to note that the permeability coefficients through the LLDPE12 and LLDPE7 annealed membranes do not differ in value, but they are significantly larger than the values obtained for these parameters in the non-annealed films. For example, in *Table 1* one can see that the permeability coefficient of oxygen in the non-annealed LLDPE7 membrane is 1.2 barrer at 25°C, but this quantity rises to 4.5 barrer, at the same temperature, in the annealed one. Since these differences may arise from variations caused by annealing in the tortuosity path and/or the solubility coefficient, the temperature dependence of the diffusion coefficient of the gases used in this study through the annealed membranes was determined. As an example, values of this quantity for the LLDPE12 membranes are shown in *Figure 3*. It is worthy to note that the diffusion coefficients of CO_2, O_2 and N_2 through the annealed membranes are slightly lower than those obtained in the thermally untreated
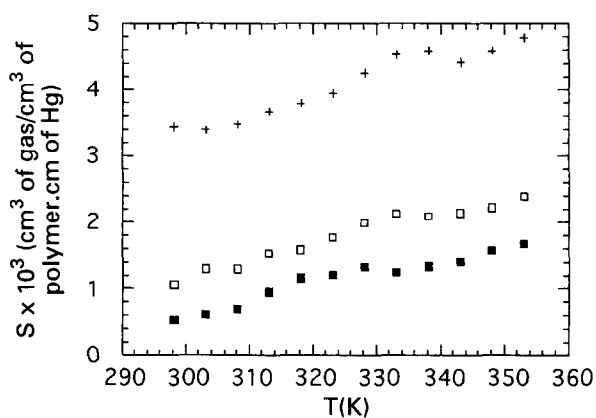
Figure 4 Temperature dependence of the solubility coefficients of CO_2 (+), O_2 (□) and N_2 (■) in annealed LLDPE12 films

ones. This can be seen in *Table 1* where for illustrative purposes the values at two temperatures of the diffusion coefficient of the gases through annealed and non-annealed LLDPE7 membranes are shown. Consequently, the rise observed in the permeability coefficient of the gases through the thermally treated membranes must be attributed to an increase in solubility caused by annealing. Values of the solubility coefficient at different temperatures were obtained from the ratio

$$S = \frac{P}{D} \qquad (4)$$

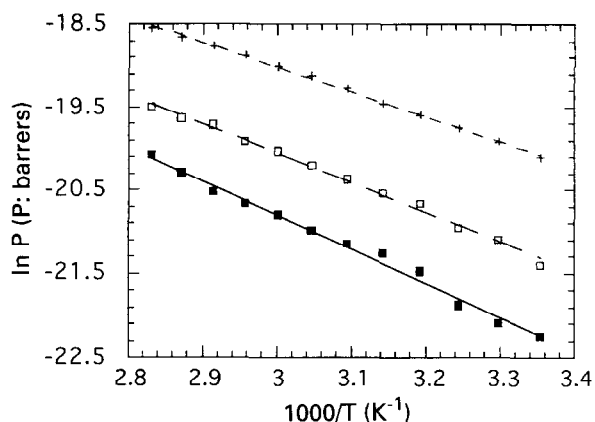and the results obtained for the LLDPE12 membrane are shown, as an example, in *Figure 4*. Contrary to what one

Figure 5 Arrhenius plots of the permeability coefficients of CO_2 (+), O_2 ($\square$) and N_2 ($\blacksquare$) for annealed LLDPE12 films

Figure 7 Arrhenius plots of the diffusion coefficients of CO_2 (+), O_2 ($\square$) and N_2 ($\blacksquare$) for annealed LLDPE12 films

Permeant and diffusive processes through isotropic barriers are thermal activated processes which obey the Arrhenius expression

$$X = X_0 \exp\left(-\frac{E}{RT}\right) \tag{6}$$

where X represents the permeability or diffusion coefficients, P and D, E becomes the activation energy of the permeability, E_P, or the activation energy of the diffusion, E_D, and X_0 is a constant (P_0 or D_0) which is characteristic of the polymer permeant system. In the analysis of the temperature dependence of the permeability coefficient through thermally untreated coextruded LLDPE films it was observed that the experimental results can be expressed by two Arrhenius plots covering, respectively, the temperature intervals 20–50°C[7] and 50–70°C. A significant decrease in activation energy of the permeability was detected between the low temperature and the high temperature intervals, that was attributed to an anomalous increase in the solubility arising from both the initiation of the melting of the smaller crystalline entities and to the uncoiling of the oriented chains in the crystalline–amorphous interface. This behaviour is not detected in the temperature dependence of the permeability of carbon dioxide, nitrogen and oxygen through the annealed samples where, as can be seen in *Figures 5* and *6*, the coefficient P obeys the Arrhenius expression in the whole temperature range (25–80°C). As shown in *Table 2*, activation energy for the permeability coefficient of the gases in the annealed films follows the trend $CO_2 < O_2 < N_2$.

Figure 6 Arrhenius plots of the permeability coefficients of CO_2 (+), O_2 ($\square$) and N_2 ($\blacksquare$) for annealed LLDPE7 films

would expect, the solubility coefficient of the gases in the annealed semicrystalline membranes used in this study slightly increases with temperature. Annealing may cause crystallites to thicken[12], that impedes gas permeation, but it also may produce melting of the less perfect crystalline entities which favours it. It is important to note that the values of the solubility coefficient of the permeants are nearly two times larger in the LLDPE7 annealed than in the LLDPE12 one. According to the dual mode theory, the solubility coefficient of the permeants in both the amorphous region and the crystalline–amorphous interfaces can be expressed by[13,14]

$$S = k_D + \frac{C'_H b}{1 + bp} \tag{5}$$

where k_D is the Henry's law constant, C'_H is the Langmuir capacity constant connected with the hole filling like mode, b is the Langmuir affinity constant and p is the pressure. Although an increase in temperature diminishes k_D and hence S, it may increase packing defects caused in the crystalline–amorphous interface thus providing sorption sites for the permeants. This latter effect together with the melting of low crystallite size entities are presumably responsible for the increase of the solubility coefficient of the permeants with temperature.
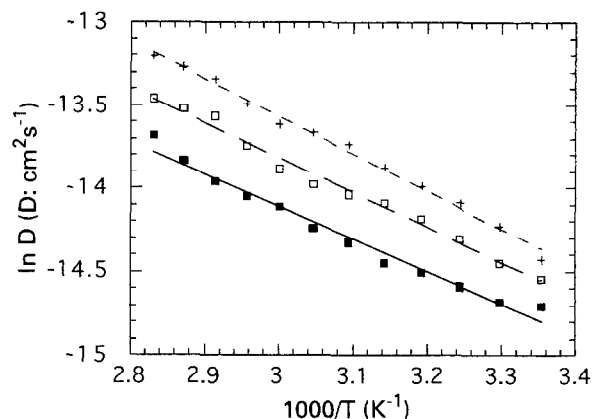
As occurs with the permeability coefficient, the temperature dependence of the diffusion coefficient of the gases in nonannealed coextruded LLDPE films is also fitted by two Arrhenius plots covering the two intervals of temperature indicated above[7]. On the contrary, a single Arrhenius plot covers the diffusion coefficient results through the whole temperature interval in the annealed membranes, as can be seen in *Figures 7* and *8* where these plots for the LLDPE7 and LLDPE12 membranes, respectively, are shown. It is worth noting that contrary to what occurs with the permeability coefficients, the apparent activation energies for the diffusants do not show a strong dependence on the nature of the gases, though the energies follow the trend

Table 2 Activation energies in kcal mol^{-1} for the permeability and diffusion coefficients of carbon dioxide, oxygen and nitrogen through annealed LLDPE7 and LLDPE12 membranes in the temperature interval 25–80°C

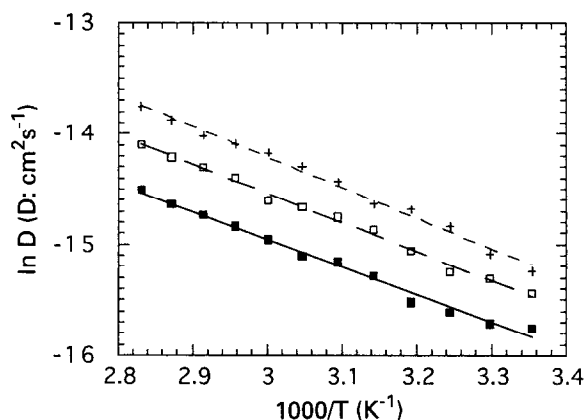| | E (kcal mol^{-1}) | | | | | |
| | Permeability | | | Diffusion | | |
Film	CO_2	O_2	N_2	CO_2	O_2	N_2
LLDPE7	5.96	7.88	10.64	5.54	5.24	5.01
LLDPE12	5.98	7.12	8.16	4.52	4.18	3.90

Figure 8 Arrhenius plots of the diffusion coefficients of CO_2 (+), O_2 (□) and N_2 (■) for annealed LLDPE7 films

$N_2 < O_2 < CO_2$ (see *Table 2*). Consequently, the heat of solution $\Delta H = (E_P - E_D)$ decreases from nitrogen to carbon dioxide. The diffusion coefficient, which reflects the speed with which the permeability coefficient reaches steady state conditions, depends on the size of the permeant and on the structure of the matrix through which diffusion takes place. Matrix effects on the diffusivity were taken into account by Michaels and Parker[2] who expressed the diffusion coefficient by

$$D = \frac{D^*}{\tau\beta} \qquad (7)$$

where D^* is the diffusion coefficient for completely amorphous polymers and, consequently, only depends on the nature of the diffusant. The parameter τ reflects the tortuosity of the path caused by the presence of crystalline entities, whereas β is mainly related with the lack of mobility in the amorphous regions close to the anchoring points in the crystals[15]. The fact that the activation energy of the diffusants in LLDPE12 is lower than in LLDPE7 suggests that the obstruction to the diffusion produced by the microstructure may be somewhat larger in the latter film.

Stern and coworkers[16–18] studied gas permeation through polyethylene membranes making use of free volume concepts based on Fujita's model[19] for diffusion of small molecules in polymers. It should be pointed out that this latter theory evolved from the theoretical work of Cohen and Turnbull[20] concerning the self diffusion of a liquid of spherical molecules. According to the free volume theory, the isothermal flow of a penetrant through a membrane of sufficient large

area and thickness l is given by[18]

$$J = P\frac{P_h - p_l}{l} = \int_{v_l}^{v_h} D\,dv \qquad (8)$$

where v_h and v_l refer to the volume of penetrants dissolved at the membranes interfaces in solution equilibrium when the pressures p_h and $p_l (< p_h)$ are maintained at the membrane interfaces. The diffusion of small molecules through semicrystalline polymers can be expressed in terms of Fujita's free volume model[19] by means of the expression

$$D = RTA_d\exp\left(\frac{B_d}{\phi_a v_f}\right) \qquad (9)$$

where ϕ_a is the volume fraction of amorphous polymer, A_d and B_d are characteristic parameters, v_f is the volume fraction of free volume and R and T are, respectively, the universal gas constant and absolute temperature. The fractional free volume depends on the hydrostatic pressure applied on the high pressure chamber, the temperature, and the penetrant concentration expressed as free volume v. Following Stern *et al.*[18] the fractional free volume can be written as

$$v_f = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p - p_s) + \gamma v \qquad (10)$$

where $v_s(T_s, p_s, 0)$ is the fraction free volume of the polymer at some reference temperature T_s and pressure p_s, $\alpha(= (\delta v_f/\delta T)_s)$ and $\beta(= \delta v/\delta p)_s)$ are, respectively, the thermal expansion coefficient and the compressibility, and $\gamma(= (\delta v_f/\delta v)_s)$ is a coefficient which defines the effectiveness of the penetrant as a plasticizer. At low pressures, such as those used in this study, equation (8) can be simplified to

$$v_f = v_{fs}(T_s) + \alpha(T - T_s) \qquad (11)$$

In this work values of the fractional free volume as a function of temperature were obtained by using the approximate relation

$$v_f(T) = \frac{v_l(T) - v_c(T)}{v_l(T)} \qquad (12)$$

where v_c and v_l represent, respectively, the specific volumes of polyethylene in the crystalline and amorphous phases and the temperature dependence of the specific volumes were assumed to be[21]

$$v_l(T) = 1.152 + 8.8 \times 10^{-4}(T - 273.15)$$

$$v_c(T) = 0.993 + 3.0 \times 10^{-4}(T - 273.15)$$

Equation (7) can be written in the logarithmic form

$$\ln\left[\frac{D}{RT}\right] = \ln A_d - \frac{B_d}{\phi v_f} \qquad (14)$$

so that the terms A_d and B_d can be obtained from the least squares fit of equation (14) to the plots of $\ln(D/RT)$ vs $1/v_f$. As can be seen in *Figures 9* and *10* where these plots are represented, respectively, for LLDPE7 and LLDPE12 films, the experimental results obey equation (9) fairly well and the values of A_d and B_d obtained for CO_2, O_2 and N_2 are listed in *Table 3*. It can be seen that the results for the A_d parameter follow the trend $N_2 < O_2 < CO_2$ in LLDPE7 membranes, and their values are nearly four times larger than those
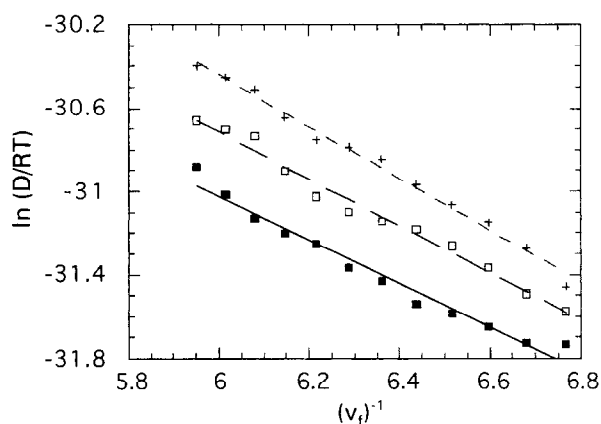
Figure 9 Semilogarithmic plot of D/RT against the reciprocal free volume for CO_2 (+), O_2 ($\square$) and N_2 ($\blacksquare$) in annealed LLDPE12 films
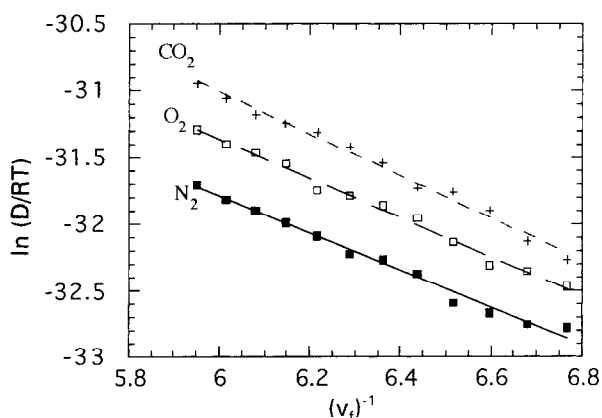
Figure 10 Semilogarithmic plot of D/RT against the reciprocal free volume for CO_2 (+), O_2 ($\square$) and N_2 ($\blacksquare$) in annealed LLDPE7 films

Table 3 Values of the free volume parameters A_d and B_d evaluated from the diffusion coefficient results

Penetrant gas	LLDPE7 films		LLDPE12 films	
	$10^{11}A_d{}^a$	$B_d{}^b$	$10^{11}A_d{}^a$	$B_d{}^b$
CO_2	42.16	0.98	10.52	0.73
O_2	16.75	1.03	4.01	0.79
N_2	6.79	1.10	1.75	0.87

[a] A_d has units of $m^2\,gmol\,s^{-1}\,J^{-1}$
[b] B_d is dimensionless

Figure 11 Permselectivity of LLDPE12 films expressed in terms of the ratio of permeability coefficients of gases, at different temperatures: $\diamond$, $P(CO_2)/P(O_2)$; $\blacklozenge$, $P(CO_2)/P(N_2)$
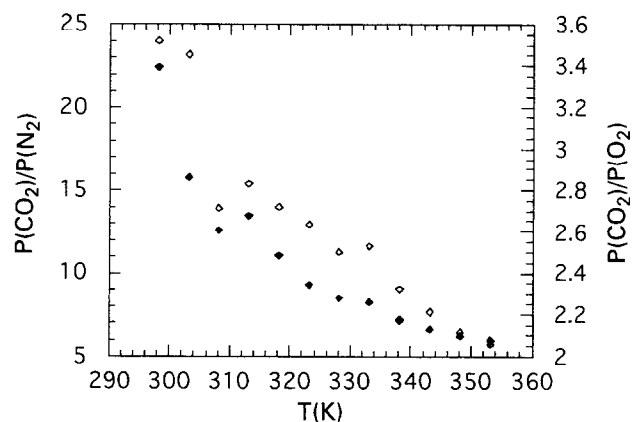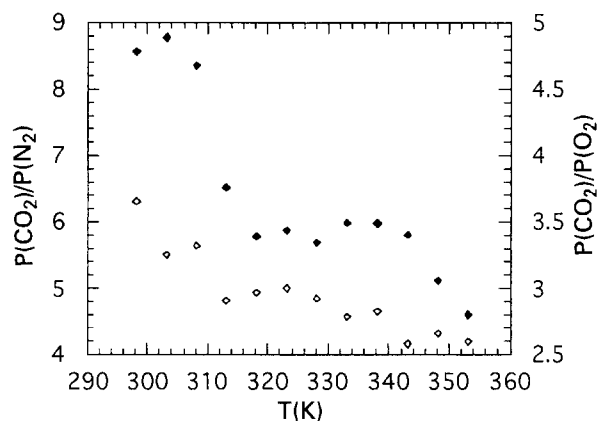

Figure 12 Permselectivity of LLDPE12 films expressed in terms of the ratio of permeability coefficients of gases, at different temperatures: $\diamond$, $P(CO_2)/P(O_2)$; $\blacklozenge$, $P(CO_2)/P(N_2)$

corresponding to this quantity in LLDPE12 films. Moreover, the parameter B_d shows the same dependence of the nature of the permeants as A_d, their values being significantly larger in LLDPE7 films than in LLDPE12 ones. These results suggest that the free volume parameters are very sensitive to the structural characteristics of the films in the sense that both A_d and B_d are larger for the films with higher birefringence. Values of these quantities have also been reported by Stern et al.[18] for the permeation of gases in polyethylene membranes. By focusing our attention on CO_2, we find that the values of A_d and B_d determined by these authors are $5.4 \times 10^{-11}\,m^2\,gmol\,s^{-1}\,J^{-1}$ and 0.40, which are significantly lower than those obtained from the diffusive results in the present work (see *Table 2*). Therefore the study of the free volume characteristics of different gas permeants in coextruded LLDPE membranes seem to suggest their orientation enhances the free volume parameters in polyethylene membranes.

The permselectivity of the LLDPE7 membrane to the CO_2/N_2 and CO_2/O_2 gas pairs is expressed in terms of the permeability ratios, $P(CO_2)/P(O_2)$ and $P(CO_2)/P(N_2)$ in *Figure 11*. In *Figure 12* these ratios are shown for the LLDPE12 membrane. In both cases a sharp decrease in the permselectivity coefficients between 290 and 310 K occurs. By comparing the results for both membranes one can see that the selectivity of CO_2 with

respect to N_2 is significantly larger in the LLDPE7 membrane than in the LLDPE12 one. However, both membranes display nearly the same permselectivity for the CO_2/O_2 gas pair.

CONCLUSIONS

Annealing of coextruded LLDPE membranes strongly increases the values of the permeability coefficients of carbon dioxide, oxygen and nitrogen through them. The fact that the values of the diffusion coefficients only undergo a slight decrease suggests that the permeability enhancement by annealing is due to the increase of the solubility of the gases in the membranes. Melting

of the smaller crystalline entities is held responsible for the slight increase of the solubility of the gases with temperature. The free volume theory gives a good account of the permeability of the gases through the annealed LLDPE membranes. Finally, film processing conditions seem to have a strong influence on the permselectivity of membranes to gases.

ACKNOWLEDGEMENT

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