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Influence of drawing on gas transport mechanism in LLDPE films

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Micrographs obtained using scanning electron microscopy reveal that the drawing of *co*-extruded linear low-density polyethylene (LLDPE) films produces numerous changes in their surface. It is necessary to analyse the effect of these changes on gas transport in LLDPE films in order to test their efficiency in the packaging industry. Permeability of He, O_2, N_2 and CO_2 has been measured in a temperature range from 25 to 85°C using the variable-pressure technique with the time-lag method. Results show that the drawing process does not have a significant effect on the gas transport mechanism. The influence of drawing on the permeability of LLDPE films to gases is discussed in the light of previous studies of diffusion and mechanical relaxation in the same material and compared with results obtained in the present work. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: LLDPE films; permeability; transport mechanism)

INTRODUCTION

Polymers and copolymers obtained from olefins, specifically polyethylene (PE) and polypropylene, have had great commercial success in the packaging industry, being the most extensively used of all thermoplastic materials. In the case of polyethylenes, there are basically two types, low-density PE (LDPE) and high-density PE (HDPE), of various grades[1]. The manufacturing processes for both types of PE are very different and their physico-chemical properties vary considerably as a consequence of their different molecular structures. The production process of a new type of LDPE at low pressure was developed 30 years ago. This new grade of PE was produced by copolymerization of ethylene with α olefins of four or six carbon atoms. This PE, known as linear LDPE (LLDPE) owing to its structure, provides better processability, high-barrier properties for packaging applications and reduced manufacturing costs. In particular, *co*-extruded LLDPE films exhibit good final properties, specifically a high tear strength and toughness. The combination of a relatively low crystallinity and a moderate orientation are mainly responsible for their special physical characteristics.

In a recent publication[2], the permeability properties and the mechanical behaviour exhibited by *co*-extruded LLDPE films oriented by drawing were studied both in the longitudinal and transverse directions. It was found that the γ- and β-relaxations do not show a noticeable dependence on the direction in which the measurements were performed. However, the mechanical α-relaxation is sensitive to the orientation because it occurs as a result of the motions in which crystalline entities intervene. The measurements carried out using an electrochemical technique over the range where the α-relaxation process takes place showed that the gas permeability coefficients through oriented films after drawing were lower than those obtained for the same gases through undrawn LLDPE films. However, the fact that the corresponding effect on the diffusion coefficient seemed to be relatively small suggested that changes in the solution-interface were responsible for the permeability decrease observed in LLDPE films which had been oriented by drawing.

In the present work, the permeability properties exhibited by the films are determined by the time-lag technique instead of the electrochemical method. In addition, the study was extended to cover a higher temperature range limited by the experimental conditions of both the device and the samples, and more gases were included in order to compare with previous work. The temperature and pressure dependence of permeability coefficients through oriented LLDPE films are studied and the results compared with those of undrawn films. In the same way, the scanning electron microscopy (SEM) technique was used in order to detect possible changes in polymer morphology produced by drawing.

EXPERIMENTAL

The raw materials used in the preparation of the films were copolymers of ethylene and 1-octene with *ca.* 8 mol% of the latter comonomer. The *co*-extruded LLDPE films were made up of three layers, where the two first layers are Dowlex 2247 ($\rho = 0.917\ \mathrm{g\ cm^{-3}}$) and the third layer is Dowlex 2291 ($\rho = 0.912\ \mathrm{g\ cm^{-3}}$). The thickness of the first, second and third layers are respectively 3.5 μm, 16 μm and 3.5 μm. Several types of *co*-extruded LLDPE films can be obtained using the same raw materials by modifying the processing conditions, such as the die exit-chill roll and die exit-frost line distances, extruder die velocity and cutting pressure.

The crystalline material fraction of the films used in the present work was determined by Raman spectroscopy, using a Ramanor U1000 double monochromator equipped with two 1800 g $\mathrm{mm^{-1}}$ planar holographic gratings. As a result of this study, we found that the values of the crystalline and amorphous fractions were 0.30 and 0.57 respectively. Accordingly, the crystalline–amorphous interface fraction amounts to 0.13. Further details about the microstructure and the processing conditions of the films have been given in a preceding paper[3].

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Measurements of the permeability of gases through the films were carried out with an experimental set-up that has been described elsewhere[3]. The measurement technique that has been adopted in the present work is the time-lag method. The polymer film is used as a diaphragm to separate two halves of a high-vacuum system and then the gas is introduced at a known pressure on one side of the film, upstream side. The gas diffuses through the film into a constant sealed volume on the downstream side and can be detected by the resulting change in pressure. Once steady-state conditions were achieved the permeability coefficient was obtained from the flow rate, with the knowledge of the film area and the input gas pressure. The measurements of pressure were performed by means of Leybold-CM3 pressure transducers.

The whole set-up was placed inside a thermostatic bath, whose temperature was measured and controlled by PT100 sensors with an accuracy of ±0.1°C. The thermostat employed was a Techne TU-16D. The measurements were performed over the temperature interval from 25 to 85°C.

The gases studied were helium, oxygen, nitrogen and carbon dioxide. The minimum purity for these gases was 99.999%, except for carbon dioxide which was 99.998%. No further purification was attempted before admission to the experimental apparatus.

The micrographs which appear in this work were taken by means of a Jeol JSM 6300 scanning electron microscope according to conventional methods.

THEORY

It is well established that the gas permeation through polymer dense membranes is described by the solution–diffusion mechanism[4,5]. The term permeation is used to describe the overall mass transport of gas across the membrane, whereas the term diffusion refers only to the movement of gas molecules inside the membrane matrix. Therefore, the term permeation comprises the solution and the molecular diffusion processes in the membrane.

The rate of permeation, as well as its pressure and temperature dependence, can be meaningfully affected by the glass transition exhibited by the polymer from which the membrane was obtained. Thus, polymers undergo a phase transformation from a soft and elastic or rubbery state to a hard and brittle or glassy state as the temperature is lowered below the glass transition temperature T_g.

For a rubbery polymer, the phenomenological permeation behaviour is relatively simple. Above the glass transition temperature, the polymer responds rapidly to changes in its condition. Thus, a change in temperature causes an immediate adjustment to a new equilibrium volume. As a result, when a gas at constant pressure is allowed to contact a rubbery membrane, the solution equilibrium is very rapidly established at the exposed membrane interface. This solution equilibrium is achieved in times very much shorter than the characteristic times involved in the diffusion of the penetrant molecules in the membrane. For very dilute penetrant solutions, the concentration c of a penetrant gas dissolved in a polymer can be related to the pressure p by Henry's law:

$$c = k_D p \tag{1}$$

where k_D is the Henry's law coefficient. In these conditions, the diffusion process satisfies Fick's first and second laws, and the diffusion coefficient is only a function of temperature.

From a practical point of view, since the concentration of the gas in the membrane is not known, it is of interest to determine the rate of gas permeation at steady-state, as well as the dependence of this rate on pressure. Steady-state permeation is achieved if, at fixed temperature, the gas pressures are maintained constant at the two membrane interfaces. In that case, Fick's first law can be written as

$$J = D\frac{\Delta c}{l} \tag{2}$$

where J is the steady-state permeation rate, D is the diffusion coefficient, Δc is the gas concentration difference between the two membrane interfaces and l is the membrane thickness.

Equations (1) and (2) then yield the relation

$$J = Dk_D\frac{\Delta p}{l} = P\frac{\Delta p}{l} \tag{3}$$

where $P \equiv Dk_D$ is a mass-transfer coefficient known as the permeability coefficient. In membrane separation processes, the applied pressure at one membrane interface is often much higher than the pressure at the opposite interface, so that equation (3) reduces to

$$J = P\frac{p}{l} \tag{4}$$

where p is the upstream pressure.

RESULTS AND DISCUSSION

The SEM technique was used to examine sample morphology. The electron microscopy was restricted to magnifications of ×500 to avoid damaging the samples. Surface examination of the undrawn films showed no prominent features, as can be seen in *Figure 1*. On the contrary, surface micrographs of oriented films after drawing reveal the presence of defects and microvoids of different sizes, as can be observed in *Figures 2 and 3*. Owing to the fact that the processing conditions provide orientation to the films, the number of these defects is larger in films subject to longitudinal drawing (direction parallel to processing orientation) than in films subject to transverse drawing (perpendicular direction). The possibility of continuous channels between defects on film interfaces has stimulated us to examine the gas transport mechanism in drawn films.

There are two distinctive mechanism for gas permeation through polymer films, i.e. (i) solution–diffusion and (ii) mass flow through holes[6]. The type of permeation can be determined by the dependence of the permeability coefficient on temperature and pressure. When the permeability exhibits a large temperature dependence, but no pressure dependence, it can been concluded that the dominant mechanism is of the solution–diffusion type. On the other hand, the gas permeation occurs by flow mass through cavities if the permeability is pressure dependent and decreases with increasing molecular weight of the gas.

Values of the permeability coefficients of He, O_2, N_2 and CO_2 through the undrawn film, measured at different temperatures, are shown in *Figure 4*. All the plots clearly demonstrate an Arrhenius temperature dependence with two differentiated intervals. The low-temperature interval extends from 25 to 55°C, whereas the high-temperature interval extends from 55 to 85°C. The values of the activation energy exhibited by the permeability coefficients are given in *Table 1*. A significant decrease in these values can be observed in going from the low-temperature to the

Figure 1 Surface scanning electron micrograph of undrawn *co*-extruded LLDPE film

Figure 2 Surface scanning electron micrograph of longitudinally oriented *co*-extruded LLDPE film

Table 1 Values of the activation energies associated with the permeability coefficients for He, O_2, N_2 and CO_2 through unstrained films and films oriented by drawing over the temperature range from 25 to 85°C

Film	Temperature interval (°C)	E_P (kJ mol^{-1})			
		He	O_2	N_2	CO_2
Undrawn film	25–55	30.8	35.6	40.8	30.5
	55–85	22.6	24.0	26.6	17.4
Longitudinally drawn film	25–55	30.7	36.9	42.4	33.1
	55–85	25.7	27.9	31.3	21.8
Transversely drawn film	25–55	31.5	36.8	39.2	33.4
	55–85	27.4	30.1	31.7	23.4

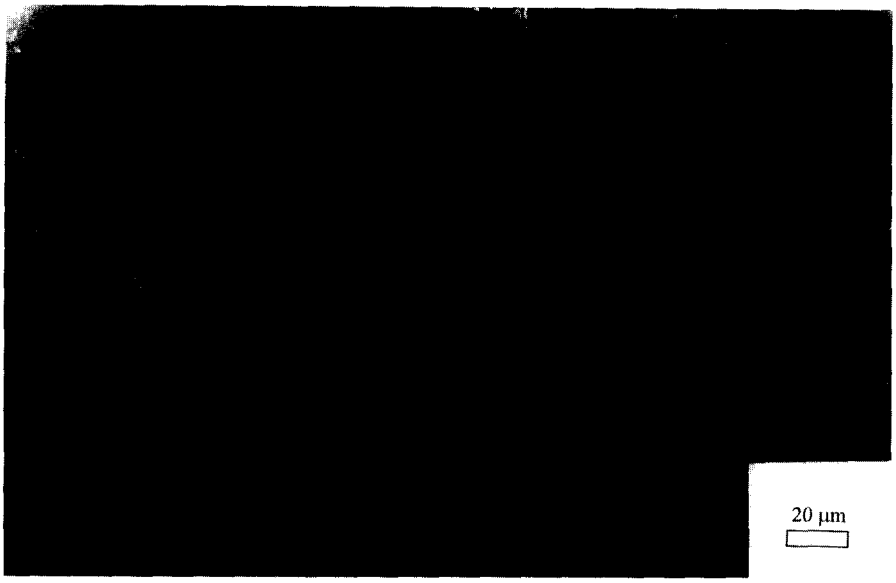

Figure 3 Surface scanning electron micrograph of transversely oriented *co*-extruded LLDPE film

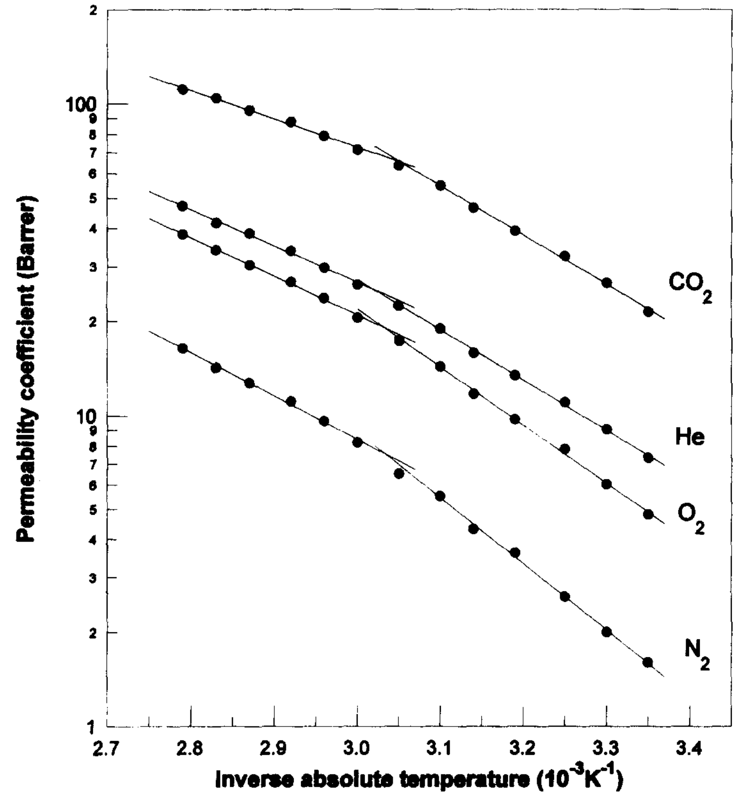

Figure 4 Arrhenius plots for the permeability coefficients of gases through *co*-extruded LLDPE film

high-temperature interval for all gases. The absence of linearity in the Arrhenius plots was associated by Compañ *et al.* to an α transition, which is usually observed in *co*-extruded LLDPE over this range of temperatures[2,3]. The α transition is a relaxation process which was attributed to molecular motions in which crystalline entities intervene. However, since this relaxation is not observed in the mechanical spectrum of single crystals of *n*-alkanes, the presence of an amorphous region is necessary to allow its development. Accordingly, Boyd has related the α-relaxation to the deformation of the amorphous region, which takes place as a consequence of reorientation within the crystallites[7,8].

The permeability coefficients for He, O_2, N_2 and CO_2, and their temperature dependence obtained for oriented films elongated by a factor of two in the direction parallel to the processing orientation, are represented in *Figure 5*. The permeability values obtained for films oriented by the same amount in the direction perpendicular to the processing orientation are shown in *Figure 6*. It is found again for both drawn films that the permeation temperature dependence follows an Arrhenius-type behaviour with two distinct temperature intervals. The extension of the two intervals is slightly different from that observed in undrawn films. Therefore, in the longitudinally drawn film the temperature at which the change of slope in the Arrhenius plots is

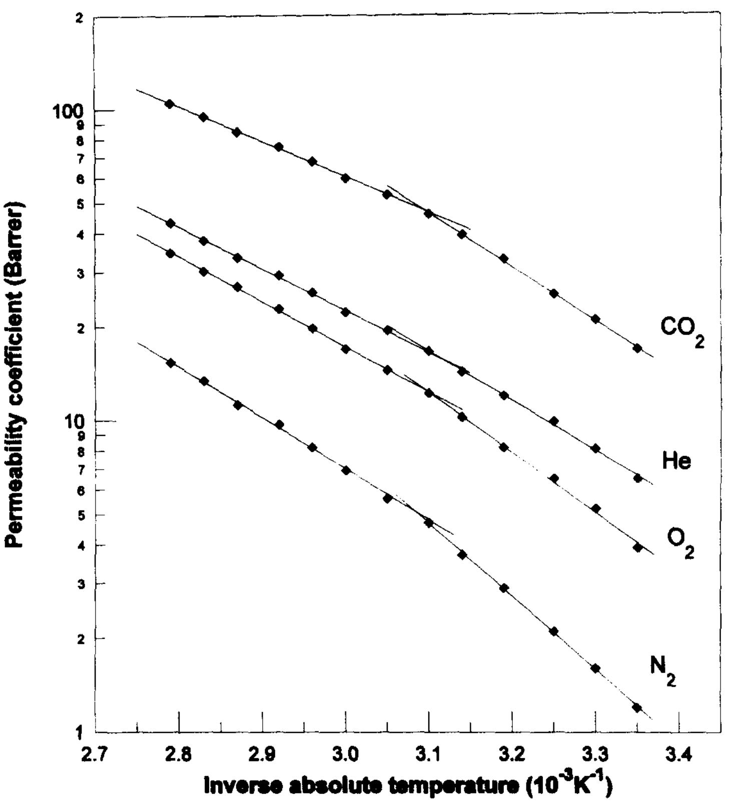

Figure 5 Arrhenius plots for the permeability coefficients of gases through *co*-extruded LLDPE film drawn in the direction parallel to the processing orientation

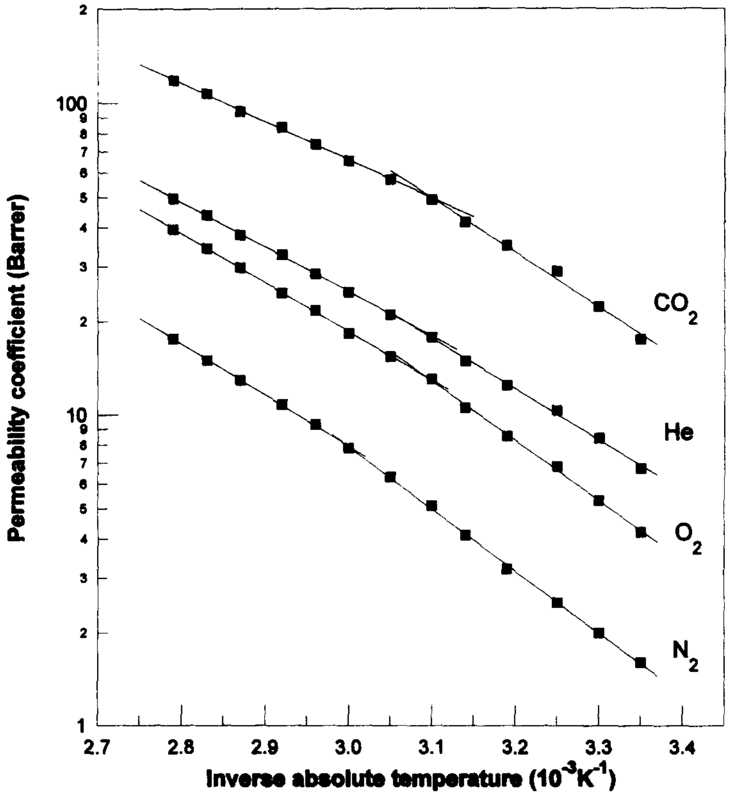

Figure 6 Arrhenius plots for the permeability coefficients of gases through *co*-extruded LLDPE film drawn in the direction transverse to the processing orientation

detected is approximately 50°C, whereas in the transversely drawn film this temperatures ranges from 50 to 60°C, depending on the gas. The values of the activation energies associated with the permeability coefficients in both oriented films are presented in *Table 1*. In this case, the decrease in the activation energies of permeation is smaller than that observed in undrawn films; however, it is still significant.

The permeability coefficients of He, O_2, N_2 and CO_2 in undrawn and drawn films were measured as a function of the applied pressure at several temperatures over the temperature range from 25 to 85°C. The results obtained in undrawn film show that the permeability does not depend on pressure over the pressure interval examined. *Figure 7* illustrates the effect of pressure on the permeability coefficient values measured at 30°C, which also exemplifies the results obtained at other temperatures. It should be pointed out that significant changes in measured permeability coefficients for gases are observed when the pressure is varied at values lower than 200 mbar[9], as can be seen in *Figure 8*. A further study of this behaviour in the low pressure interval is currently being made and will be discussed in a subsequent paper. The permeability measurements made with longitudinally and transversely oriented films do not show any discernible effect of pressure over the pressure interval studied. The values of permeability obtained for measurements carried out at 30°C that exemplify this behaviour are presented in *Figures 9* and *10*.

The plots of permeability coefficients against the molecular weight of the permeating gas showed no

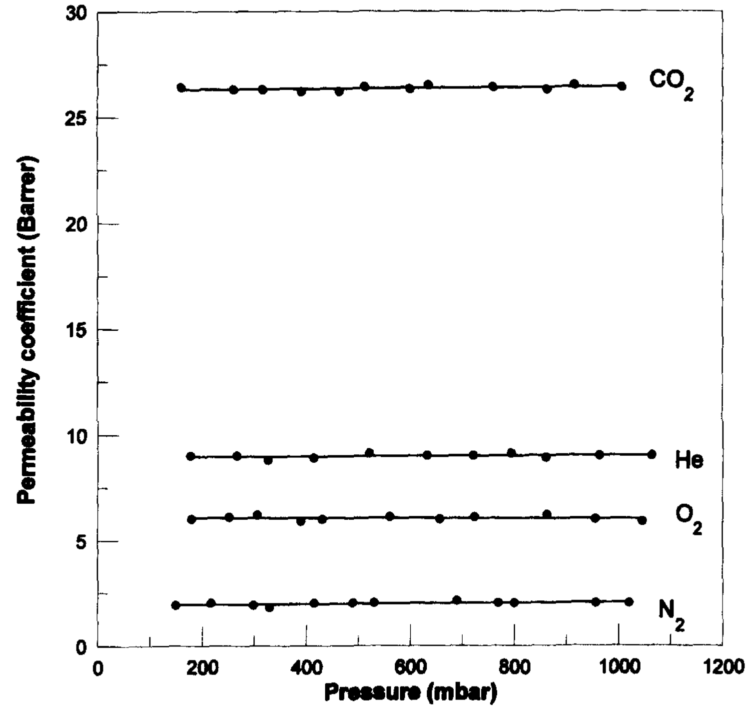

Figure 7 Permeability coefficients of gases through *co*-extruded LLDPE films at 30°C as a function of the applied pressure

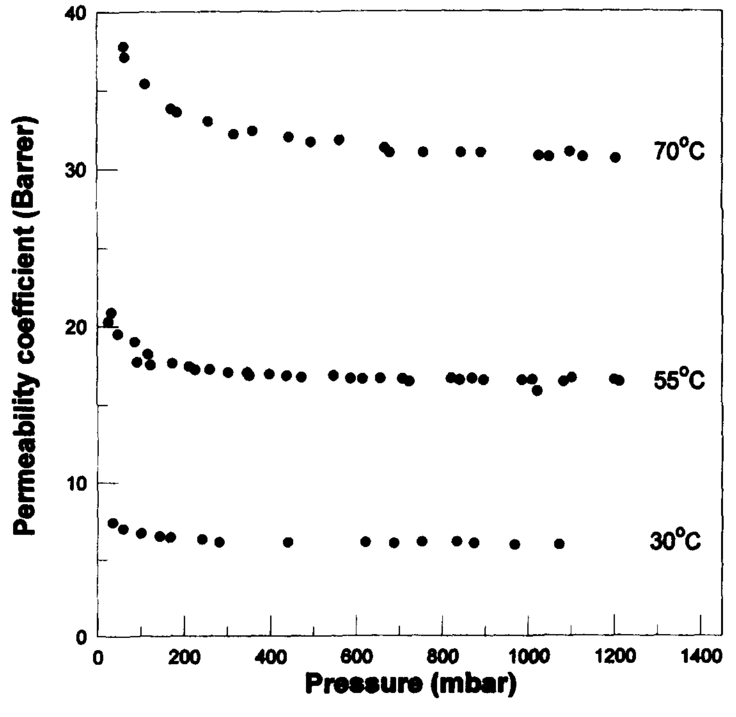

Figure 8 Permeability coefficients of O_2 through *co*-extruded LLDPE films at several temperatures as a function of the applied pressure

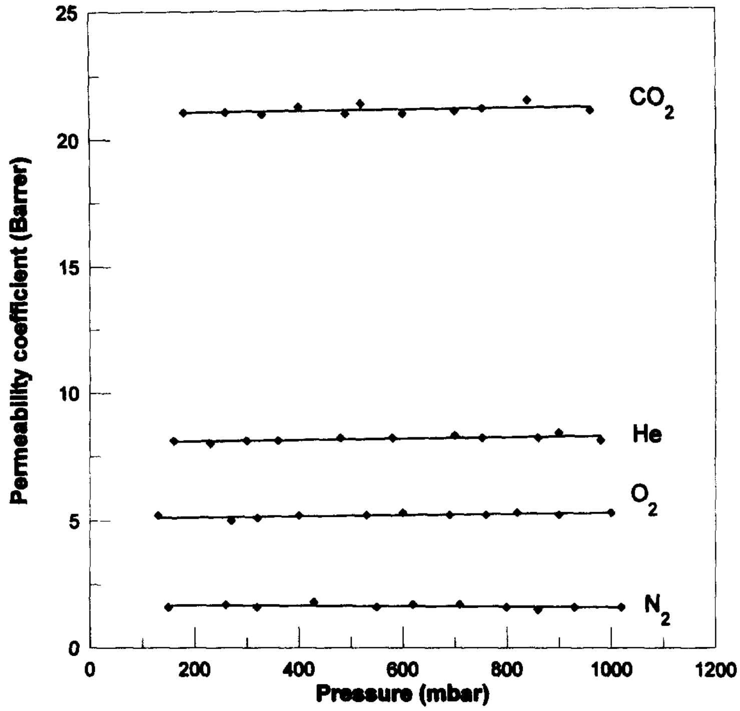

Figure 9 Permeability coefficients of gases through *co*-extruded longitudinally drawn LLDPE films at 30°C as a function of the applied pressure

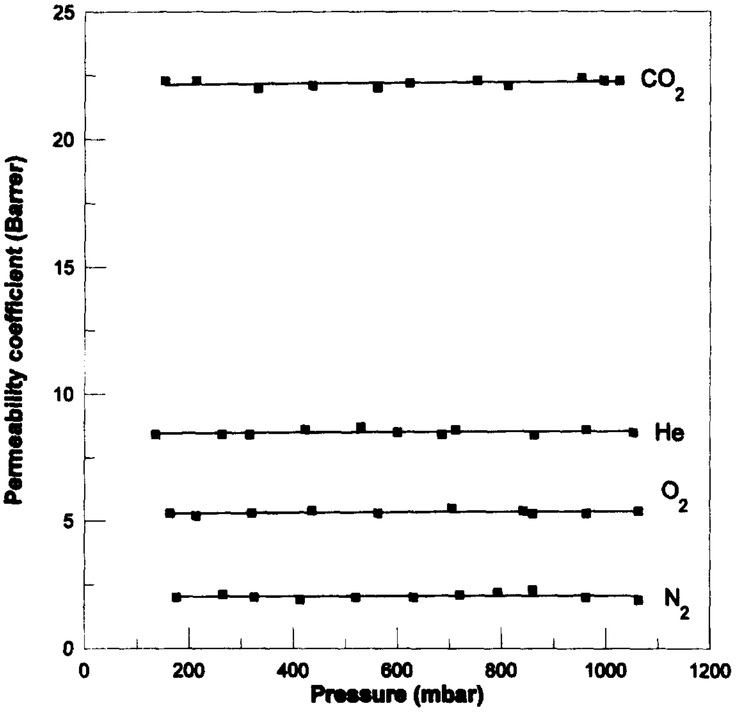

Figure 10 Permeability coefficients of gases through *co*-extruded transversely drawn LLDPE films at 30°C as a function of the applied pressure

systematic dependence in all cases. *Figures 11–13*, obtained with the values measured at 30°C, are presented as an example.

Finally, all the results obtained indicate that the gas permeation through films oriented by drawing occurs by the same mechanism as in undrawn films, i.e. the solution–diffusion mechanism.

Gas permeabilities are compared for unstrained films and films oriented by drawing in *Figure 14*. The results show that, over the temperature interval examined, the permeability coefficients are slightly decreased by drawing. The reduction in permeability is approximately the same for all gases and it never exceeds 25%. Departure from this behaviour appears at the highest experimental temperatures, at which the values of permeability in transversely drawn film are somewhat larger than those of the undrawn and longitudinally drawn films. Ref. 2, employing electrochemical techniques in order to determine the permeation properties of the same polymeric material, shows the same behaviour as reported in the present study. In that case, the permeation study was carried out only at the low temperature interval, and the values of permeability were

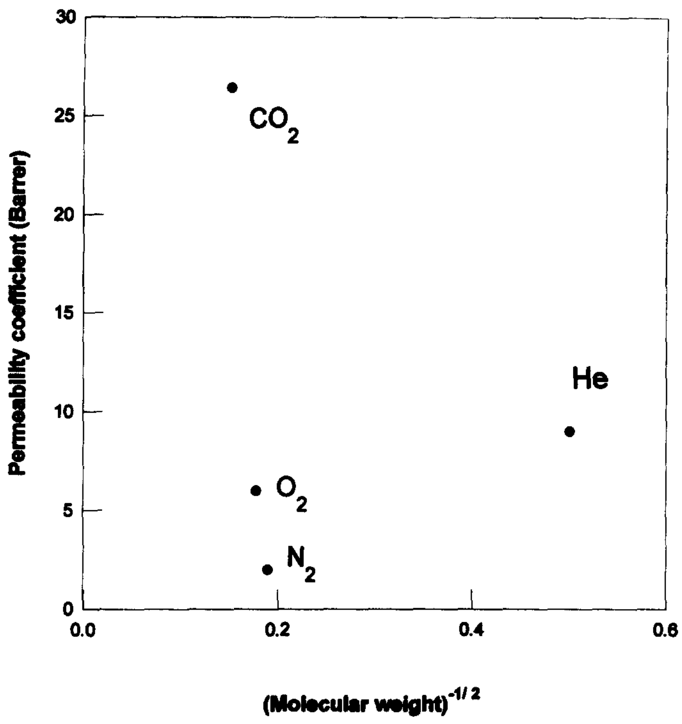

Figure 11 Permeability coefficient through *co*-extruded LLDPE film at 30°C: dependence on molecular weight of permeant gas

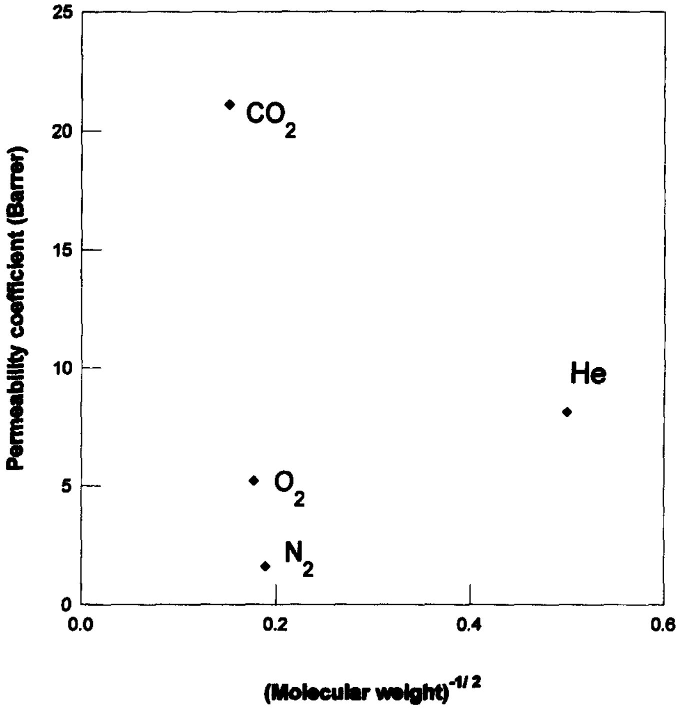

Figure 12 Permeability coefficient measured at 30°C through *co*-extruded LLDPE film drawn in the direction parallel to the processing orientation: dependence on molecular weight of permeant gas

reduced by approximately the same extent as a result of drawing. This reduction was associated, on the basis of a contribution from Holden *et al.*[10], with the fact that, on drawing, the initial spherulitic structure transforms into a new microfibrillar structure. Microshear processes at the surface of the fibrils produce extended molecules which also make possible the appearance of an increasing orientation in the crystalline–amorphous interface. As a result of this improvement in molecular order the diffusion coefficients decrease, thus decreasing the permeability coefficients.

Both longitudinal and transverse drawing of LLDPE films cause virtually no change in activation energies of permeation in the low-temperature interval. This behaviour has been observed in oriented PE film over the same range of temperature by Holden *et al.*[10], and has been related to differences in accessibility and diffusion path lengths without changes in the energy requirements to jump between sites. It is worth noting, on the other hand, the increase in activation energies shown by the permeability coefficients in both drawn films over the high-temperature

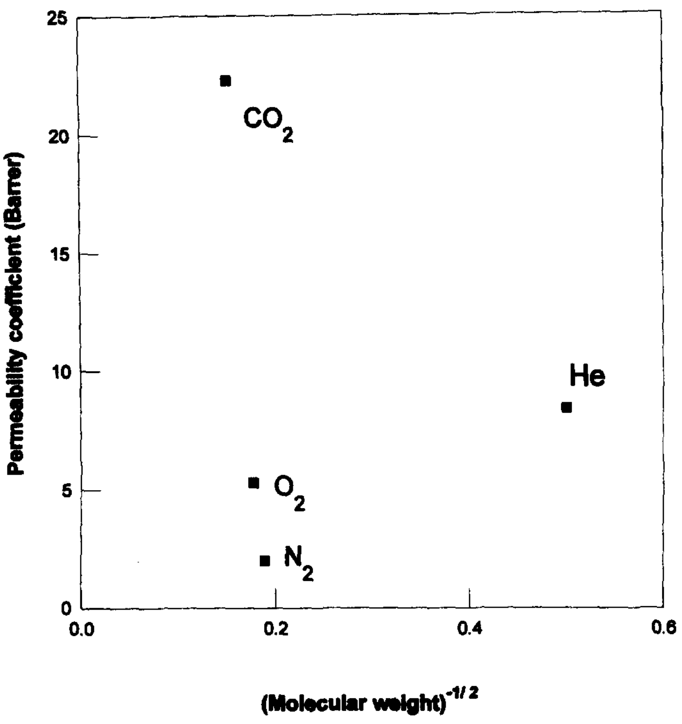

Figure 13 Permeability coefficient measured at 30°C through *co*-extruded LLDPE film drawn in the direction transverse to the processing orientation: dependence on molecular weight of permeant gas

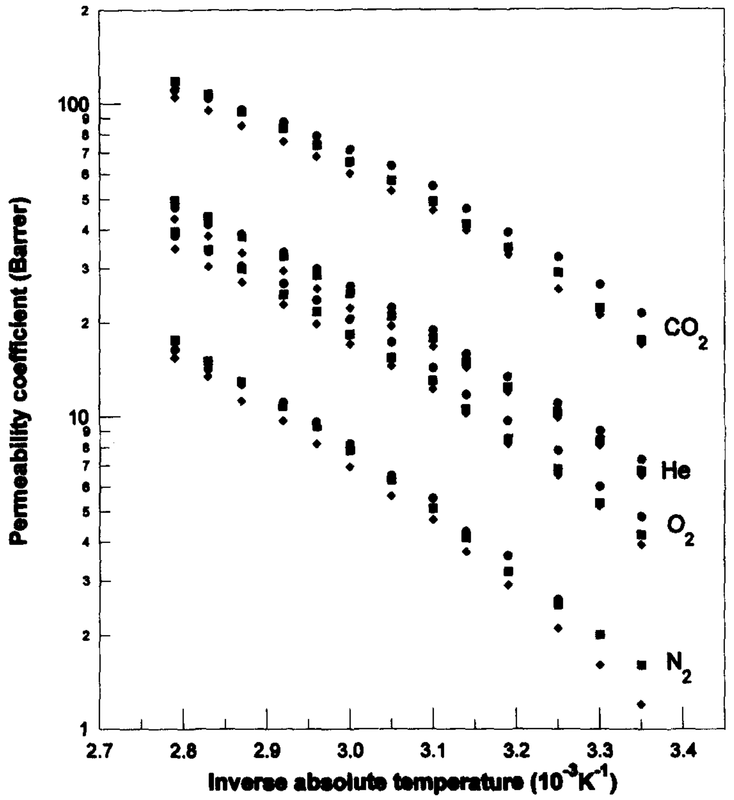

Figure 14 Arrhenius plots for the permeability coefficients of gases through *co*-extruded LLDPE film (●) and through films drawn in the directions parallel (◆) and transverse (■) to the processing orientation

interval, compared with that obtained for the permeability of undrawn films over the same temperature interval. This increase produced by the drawing process may be interpreted, first, as a consequence of an increase of the jump length for gas diffusion caused by the reduction in the number of available sites[11] and also to strain-imposed restraints on the molecular mobility in non-crystalline regions of the polymer.

The selectivity of a polymer film towards two different penetrant gases may be expressed in terms of an 'ideal' separation factor, which is the ratio between the permeability coefficients of the two gases through the film. However, the actual degree of separation for a given gas mixture and polymer film is somewhat lower, because it depends on the up- and down-stream pressure ratio, the composition of the mixture, the stage 'cut' and the flow pattern of the gas streams on the two film interfaces[12]. Assuming that the permeability coefficients for the mixture components are the same as those of the pure components, which is usually valid in the case of small gas molecules and polymers in the rubbery state such as that studied in the present work, the separation factors in undrawn LLDPE films over the 25–85°C interval were calculated from the results obtained and are shown in *Table 2*. The separation factor values, and their decrease with increasing temperature, are of the same order as those reported in the literature for other PE films. By comparing these values with those obtained in oriented films, given in *Tables 3* and *4*, it could be concluded that

Table 2 Values of the ideal separation factors in *co*-extruded LLDPE films over the temperature interval from 25 to 85°C

T (°C)	CO_2/He	CO_2/O_2	CO_2/N_2	He/O_2	He/N_2	O_2/N_2
25	2.9	4.4	13	1.5	4.4	2.9
30	3.0	4.4	13	1.5	4.2	2.9
35	2.9	4.1	12	1.4	4.1	2.9
40	2.8	4.0	11	1.4	3.8	2.7
45	2.8	4.0	10	1.3	3.6	2.6
50	2.8	3.7	9.9	1.3	3.5	2.7
55	2.7	3.6	9.0	1.3	3.3	2.5
60	2.7	3.6	8.6	1.3	3.2	2.4
65	2.7	3.4	8.0	1.3	3.0	2.4
70	2.6	3.2	7.5	1.2	2.9	2.3
75	2.4	3.1	7.3	1.2	2.9	2.4
80	2.5	3.0	6.8	1.2	2.8	2.3
85	2.4	3.0	6.8	1.2	2.8	2.3

Table 3 Values of the ideal separation factors in *co*-extruded LLDPE films oriented by longitudinal drawing over the temperature interval from 25 to 85°C

T (°C)	CO_2/He	CO_2/O_2	CO_2/N_2	He/O_2	He/N_2	O_2/N_2
25	2.9	4.5	14	1.6	4.8	2.9
30	2.8	4.4	13	1.5	4.1	2.7
35	2.9	4.3	12	1.5	4.2	2.8
40	2.8	4.0	11	1.4	3.9	2.6
45	2.8	3.9	11	1.3	3.6	2.7
50	2.8	3.8	9.5	1.2	3.4	2.5
55	2.7	3.6	8.8	1.3	3.2	2.4
60	2.7	3.5	8.3	1.3	3.1	2.3
65	2.6	3.4	8.1	1.3	3.0	2.4
70	2.6	3.2	7.9	1.2	3.1	2.3
75	2.4	3.1	7.3	1.2	2.9	2.4
80	2.5	3.0	6.8	1.2	2.8	2.3
85	2.5	3.1	6.6	1.2	2.8	2.3

Table 4 Values of the ideal separation factors in *co*-extruded LLDPE films oriented by transverse drawing over the temperature interval from 25 to 85°C

T (°C)	CO_2/He	CO_2/O_2	CO_2/N_2	He/O_2	He/N_2	O_2/N_2
25	2.9	4.5	14	1.6	4.8	2.9
30	2.9	4.5	13	1.5	4.5	2.8
35	2.8	4.3	12	1.4	4.1	2.8
40	2.8	4.0	12	1.4	4.0	2.6
45	2.7	3.9	11	1.3	3.8	2.7
50	2.8	3.8	9.4	1.3	3.5	2.5
55	2.7	3.7	8.7	1.3	3.3	2.5
60	2.7	3.5	8.4	1.2	3.1	2.3
65	2.6	3.4	8.1	1.3	3.1	2.4
70	2.5	3.2	7.8	1.2	3.0	2.4
75	2.4	3.1	7.5	1.3	2.9	2.4
80	2.5	3.0	6.9	1.2	2.8	2.3
85	2.4	3.0	6.7	1.2	2.8	2.3

both longitudinal and transverse drawing do not modify the separation factor except for a slight change with temperature.

It should be pointed out that the behaviour shown by *co*-extruded LLDPE membranes differs from that obtained for other polyolefin membranes. A detailed study of the barrier properties of highly drawn PE films was carried out by Holden *et al.*[10]. In this work, a large reduction in both diffusivity and permeability was observed with increasing draw ratio. This reduction was interpreted in terms of a greater blockage of the available diffusion paths on drawing. In the same way, a substantial reduction of the diffusion of organic vapours in drawn PE films was reported by Williams and Peterlin[11], which was considered as being a direct consequence of the denser packaging and ordering in the amorphous regions produced by the drawing process. Shimizu *et al.*[13], on the other hand, reported that extension of polypropylene films leads to an increase in permeability. This change in transport properties was associated with an increase in the specific volume accompanied by the creation of voids during the drawing process. In the present work, drawing has only a small effect on gas permeability through *co*-extruded LLDPE films. The small decrease observed in permeability properties of the oriented LLDPE films, which has been related to an increase of molecular orientation in the polymer film, and their excellent mechanical properties, reported earlier, make feasible a widespread use of *co*-extruded LLDPE films in the packaging industry.

CONCLUSIONS

Analysis of the permeability coefficients dependence on pressure and temperature indicates that the transport mechanism in longitudinally and transversely oriented films is the solution–diffusion type. This result indicates that the defects produced in the film surface on drawing are not interconnected. Moreover, the gas permeability through drawn *co*-extruded LLDPE films is an activated thermal process, with a change in the corresponding activation energy in the same temperature range as that detected in undrawn films.

In general, orientation produces a slight decrease of the gas permeability through the *co*-extruded LLDPE films. This reduction seems consistent with earlier transport studies for the same polymer films, and it is associated with microstructural changes produced in the drawing process. The maintenance of diffusive properties exhibited by the films under drawing, permits its use as an excellent separation barrier in the packaging industry.

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