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Mechanical relaxations and diffusional characteristics of coextruded films prepared from copolymers of ethylene-1-octene

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The relaxation behaviour of coextruded linear low-density polyethylene (LLDPE) films, prepared from copolymers of ethylene-1-octene, is reported. The spectra, expressed in terms of loss tan δ, present a γ relaxation of lower intensity than that exhibited for conventional low density polyethylene of the same crystallinity, followed, with increasing temperature, by a β relaxation process that appears as an ostensible shoulder of the first of two relaxation processes, denoted by α' and α'', detected in the α region. The β relaxation, which is believed to be produced by motions taking place in the amorphous and interfacial regions, appears as a well developed peak when the results are expressed in terms of the loss relaxation modulus. Whereas the α' relaxation is believed to be associated with motions in which the crystalline entities intervene, the α'' peak seems to be related to the crystallites thickening. The study of the characteristics of CO_2 diffusion through the films shows that the permeability coefficient undergoes a significant increase between 27 and ~52°C, followed by a plateau in which the permeability remains nearly constant. The permeability of oxygen follows similar trends, although the changes of this parameter with temperature are less ostensible. Gas diffusion through the films may not be a simple activated process since it seems to be governed by complicated molecular motions involving crystalline entities.

(Keywords: LLDPE films; mechanical relaxation; diffusion)

INTRODUCTION

The rate of permeation through polymer films is governed by the size of the permeating molecules and the dynamics of the molecular chains[1,2], with the latter effect being straightforwardly related to the structure of the chains. The effect of chain dynamics on the diffusional characteristics of the films becomes particularly clear if it is considered that below the glass transition temperature (T_g), where the chains are mainly frozen and only short-range motions are allowed, the diffusion of gases is severely restricted with respect to what occurs above T_g, where long-range motions take place. As a consequence, molecular chains with bulky side groups that hinder the conformational transitions about the backbone may exhibit relatively low diffusional characteristics, even at moderately high temperatures[3–8]. The chemical structure also affects the microstructure of the films, i.e. the development of crystalline order[9,10]. The presence of a crystalline phase influences both the sorption of the gas on the film surface and its transport through it. It should be noted that transport is likely to occur almost exclusively through the amorphous phase where short-range (below T_g) or long-range (above T_g) conformational transitions are permitted that create holes through which the gas molecules can randomly jump. Macroscopic flow under a concentration gradient can then be viewed as the result of a greater amount of molecular jumping from positions of higher concentration to positions of lower concentration, rather than vice versa.

Coextruded linear low-density polyethylene (LLDPE) films exhibit good ultimate properties, specifically a high tear strength and toughness. Owing to their excellent mechanical properties, these films are of great commercial success in the packaging industry. The combination of a relatively low crystallinity and a moderate orientation are mainly responsible for their special physical characteristics. This work addresses the study of the permeation characteristics of coextruded

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LLDPE and, for that purpose, pertinent experiments were conducted at several temperatures above 0°C by which the temperature dependence of both the permeability and diffusion coefficients of oxygen and carbon dioxide are determined. Although crystalline regions merely act as barriers impeding the flow, their effect on the permeation will also depend on the crystalline–amorphous interfaces which are influenced by the molecular orientation in the samples. It should be pointed out in this respect that a thorough study on the effect of orientation on the gas permeability of polyethylene, carried out by Holden *et al.*[10], showed a large reduction in the diffusion coefficient with an increasing draw ratio. Therefore, it is expected that diffusion measurements will provide a sensitive way to detect structural changes, particularly in the non-crystalline region of the coextruded films used in this study.

The morphological features of polyethylene films are also reflected in their mechanical relaxation spectra. It should be pointed out, however, that in spite of the wealth of information available on the dynamic mechanical behaviour of these systems, the interpretation of the data has been highly controversial. The reason does not lie only in the interpretation of the spectra, but also in the fact that the available data may differ because of differences in thermal history, instrumentation, etc. Therefore, in this work the dynamic mechanical behaviour of the LLDPE films used in the gas transport measurements is studied, giving special emphasis to the interpretation of the spectra for the temperature intervals over which the permeation studies were performed, with the aim of comparing the changes occurring in the spectra with those observed in the permeability measurements.

EXPERIMENTAL

Characteristics of the LLDPE films

The raw materials used in the preparation of the films were copolymers of ethylene-*co*-octene with a content of ~8% of the latter comonomer. Two LLDPE films, made up of three layers, i.e. A(15%)A(70%)B(15%), in which the layers A and B are Dowlex 2247 ($\rho = 0.917\,\mathrm{g\,cm^{-3}}$) and Dowlex 2291 ($\rho = 0.912\,\mathrm{g\,cm^{-3}}$), respectively, were used in this study. The two films, denoted by LLDPE1 and LLDPE2, were obtained by coextrusion using the same raw materials, but different processing conditions.

The thermal behaviour of the films was analysed by using a Perkin–Elmer DSC-4 calorimeter at a heating rate of 8°C min^{-1}. The thermograms of the films exhibit a simple peak that corresponds to the melting of the crystalline phase whose departure from the baseline and maximum are located, respectively, at 60 and 120°C. The degree of crystallinity of the films, determined from the melting endotherms by assuming that the melting enthalpy is 960 cal (mol CH_2)$^{-1}$, was found to be 0.25 and 0.24 for LLDPE1 and LLDPE2, respectively. The crystallinity of both films was also determined by Raman spectroscopy, using a Ramanor U 1000 double monochromator equipped with two 1800 g mm^{-1} planar holographic gratings. Excitation was provided by ~100 mW of the 514.5 nm radiation of a Spectra Physics series 2000 Ar$^+$ laser. The plasma lines were eliminated by using an Applied Photophysics premonochromator and the scattered light was collected using 90° geometry. The spectra present two peaks centred at 1418 and 1077 cm^{-1} which are considered to be associated, respectively, with the crystalline and amorphous phases[11]. By comparing the intensities of these peaks with that of the peak located at 1296 cm^{-1} (independent of the morphology of the films) one finds that the crystallinity/amorphous fractions of the LLDPE1 and LLDPE2 films are 0.24/0.65 and 0.24/0.60, respectively. Accordingly, the fraction of interfacial material for LLDPE1 and LLDPE2 amounts to 0.11 and 0.16, respectively. Further details about the microstructure of the films will be given in a subsequent paper.

As a result of the processing conditions, the films are oriented in the drawing direction and, as a consequence, they exhibit birefringence. This parameter was measured with an Amplival Pol microscope at room temperature. The values of $10^3\Delta n$ amount to 1.4 and 2.86, respectively, for the LLDPE1 and LLDPE2 films used in this study.

Dynamic experiments

The storage relaxation modulus, E', and the loss $\tan\delta$ of the films were measured with a PL-DMTA Mark II apparatus by using the double cantilever method in flexion. The experiments were carried out at five frequencies (0.1, 0.3, 1, 3 and 10 Hz) over the temperature interval −140 to 100°C. The measurements proceeded from low to high temperatures, at a heating rate of 1°C min^{-1}.

Permeability measurements

Measurements of the permeability of oxygen and carbon dioxide through the films were carried out with a familiar experimental set-up, placed inside a thermostat bath, which is shown schematically in *Figure 1*. After achieving a vacuum throughout all of the experimental device, gas from a reservoir inside the thermostat was allowed to flow into the chamber A (of volume V_A), so that at the beginning of the experiment one of the surfaces of the film is in contact with the permeant at both the temperature T and pressure p_0 of interest, while the other side is in contact with the chamber B (of volume V_B) which is *in vacuo*. The transport of gas through the film was measured by a pressure sensor located in chamber

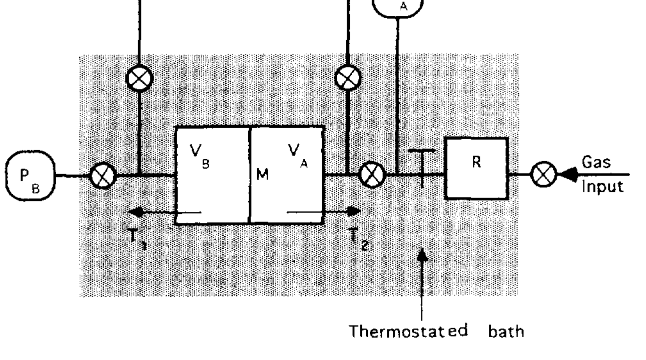

Figure 1 Experimental set-up for permeability measurements: T_1 and T_2 represent temperature sensors, the symbol ⊗ represents a valve, P_A and P_B are pressure sensors, and R is the gas reservoir, while V_A and V_B represent the volumes of chambers A and B, respectively

B, and once steady-state conditions were achieved the apparent permeability coefficient was obtained from the slope of the straight line of the plots of p *versus* t. The permeation measurements were performed over the temperature interval from 13 to 60°C, while the pressure p_0 in the subsystem A was kept at 132 ± 1 mmHg ($(0.1759 \pm 0.0133) \times 10^5$ Pa) in all of the experiments.

RESULTS

Diffusional

The transport of gases through membranes is generally expressed in terms of the permeability P and the apparent diffusion coefficient D. This last quantity can be obtained from Fick's second law as follows:

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

which relates the change of concentration c of permeant with time for unidirectional flow in the x-direction. The general solution of this relationship gives the quantity, $Q(t)$, of gas diffusing at time t as follows[12,13]:

$$Q(t)=\frac{Dc_0 t}{l}-\frac{lc_0}{6}-\frac{2lc_0}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) \tag{2}$$

where C_0 is the gas concentration in the high pressure reservoir and l is the thickness of the film. Once steady-state conditions are obtained, equation (2) approaches the linear relationship given by the following:

$$Q(t)=\frac{Dc_0}{l}\left(t-\frac{l^2}{6D}\right) \tag{3}$$

The permeability can be obtained from $\mathrm{d}Q(t)/\mathrm{d}t$, whereas D is determined by the lag method suggested by Barrer[14], as follows:

$$D=\frac{l^2}{6\theta} \tag{4}$$

where θ, the time lag, corresponds to the intercept on the time axis. The permeability coefficient, P, is usually determined by means of the following relationship:

$$P=\frac{273}{76}\left(\frac{Vl}{ATp_0}\right)\left(\frac{\mathrm{d}p(t)}{\mathrm{d}t}\right) \tag{5}$$

where p_0 is the pressure of penetrant gases in the entrance reservoir (~ 132.0 mmHg ($\sim 0.1759 \times 10^5$ Pa) in this study), $\mathrm{d}p(t)/\mathrm{d}t$ is the rate of pressure change measured by the pressure sensor connected to the low-pressure chamber shown in *Figure 1*, V is the volume of this chamber, l is the film thickness (~ 25 μm), A is the effective film area and T is the temperature in K. The unit used to express the permeability coefficient is the barrer (1 barrer $= 10^{-10}$(cm^3 (STP) cm)/(cm^2 s cm of Hg)).

The measurements of P and D were quite well reproducible, with the standard deviations being $\pm 3\%$ and $\pm 12\%$, respectively. Once P and D are known, the solubility coefficient S can be evaluated by using the following relationship:

$$S=\frac{P}{D} \tag{6}$$

The curves depicting the temperature dependence of the permeability coefficient of both O_2 and CO_2 through the LLDPE1 and LLDPE2 films are shown in *Figures 2* and *3*, respectively. Although the values of P for oxygen are significantly lower than those corresponding to CO_2, the shape of the curves is more or less similar in both cases. Thus by looking at the changes observed in the slopes of the P *versus* T plots, two regions can be differentiated, intersecting at ~ 52°C, when the penetrant is oxygen with similar changes being observed for CO_2. It should be noted that the apparent permeability is almost insensitive to temperature in the second region.

Values of the apparent diffusion coefficient, D, of O_2 and CO_2 through the LLDPE1 and LLDPE2 films are also plotted as a function of temperature in *Figures 2* and *3*, respectively. The curves for CO_2 show a slight increase in the value of D with T up until a temperature of ~ 52°C, followed by a steep increase in this quantity above this temperature. For oxygen, this change is observed at temperatures above 67°C. The complicated pattern exhibited by the temperature dependence of both the apparent permeability and the diffusion coefficient can also be seen in the temperature variation of the solubility coefficient.

Dynamic mechanical

Owing to experimental difficulties related to the bending of thin films, the dynamic mechanical experiments

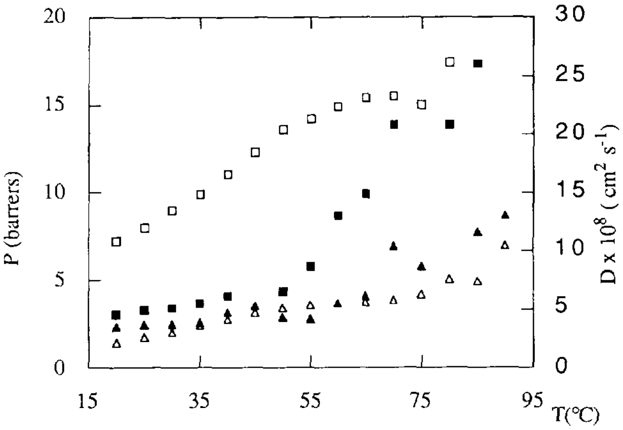

Figure 2 Temperature dependence of the permeability coefficient of O_2 (△) and CO_2 (□) for LLDPE1 films. The filled symbols refer to values for the corresponding diffusion coefficients

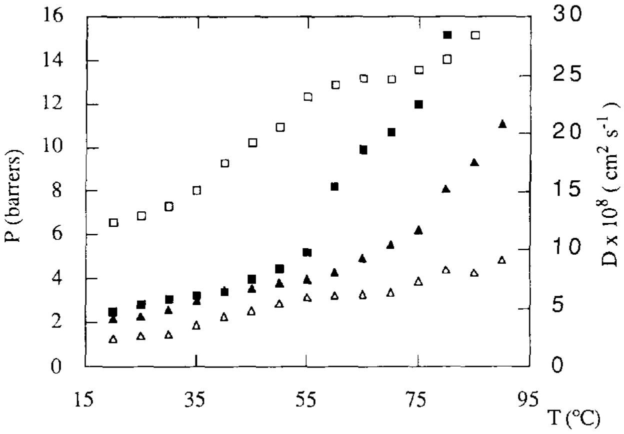

Figure 3 Temperature dependence of the permeability coefficient of O_2 (△) and CO_2 (□) for LLDPE2 films. The filled symbols represent values for the corresponding diffusion coefficients

were performed on strips made up of LLDPE films that had been firmly stuck together. The thickness effect on both the storage relaxation modulus and the loss tangent is depicted in *Figures 4* and *5*, respectively, where it can be seen that although the values of the loss are slightly dependent on the thickness of the strips, the locations of the peaks do not show any thickness dependence. The results obtained for the strips with a thickness of 0.45 mm will be used in further experiments. A close inspection of the loss tan δ *versus* T plot reveals the presence of a relaxation γ, centred at ~ 120°C, followed by an ostensible β absorption that appears as a shoulder of two or more of the relaxation processes occurring above 0°C.

DISCUSSION

It is a well known fact that high-, low-, and linear low-density polyethylene, usually represented as HDPE, LDPE and LLDPE, respectively, present three main relaxations approximately extending from -120 to -70°C (γ), from -70 to 10°C (β) and from 10°C upwards (α)[15,16]. The location of the maxima of the corresponding peaks appearing in the loss modulus *versus* temperature plots seems to be different for these polyethylenes. Thus the temperature T_α at which the maximum of the α peak for LLDPE is located (~30°C) is intermediate to that of HDPE (~52°C) and LDPE (~18°C). The fact that the intensity of the α absorption for HDPE is significantly larger than that of the low-density polyethylenes suggests that the α peak is representative of the crystalline phase and, consequently, it should originate from certain types of motion in the crystal[17-19]. Although during the α relaxation stage the chains in the crystal may undergo chain rotation, translation and twist, results obtained for high-molecular-weight paraffins seem to show that the crystals, by themselves, do not 'produce' the α process[20] and, consequently, chain folding is necessary for the occurrence of this absorption. Accordingly, the α relaxation has been attributed to motions in the interfacial regions, rather than motions in the amorphous phase[21,22].

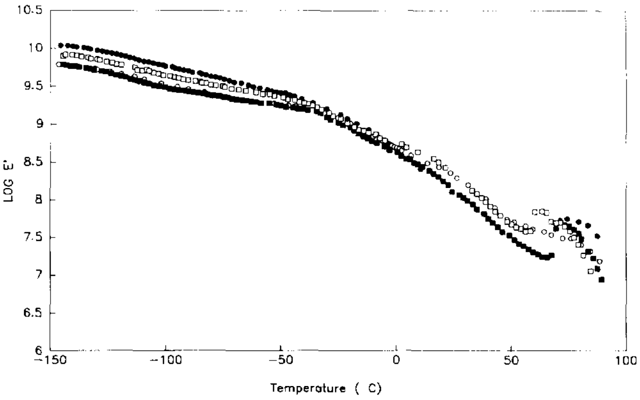

Figure 4 Temperature dependence of the storage relaxation modulus (in Pa) for strips of LLDPE2 films that have been stuck together, measured for different thicknesses: (●) 0.38; (□) 0.45; (■) 0.61; (○) 0.80 mm

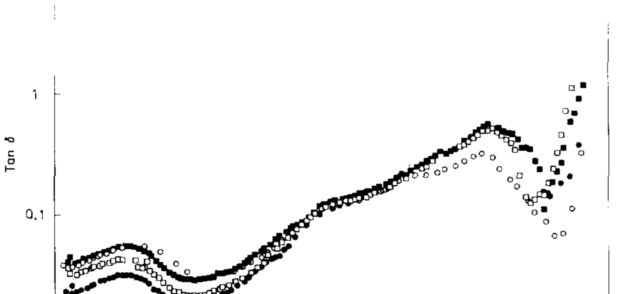

Figure 5 Variation in the value of loss tan δ with temperature for strips of LLDPE2 films that have been stuck together, measured for different thicknesses: (●) 0.38; (□) 0.60; (■) 0.61; (○) 0.80 mm

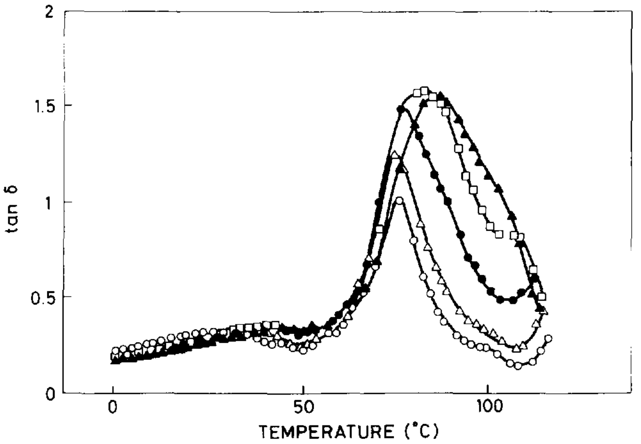

Figure 6 Values of tan δ as a function of temperature for LLDPE1 films measured at different frequencies: (○) 0.1; (△) 0.3; (●) 1; (□) 3; (▲) 10 Hz

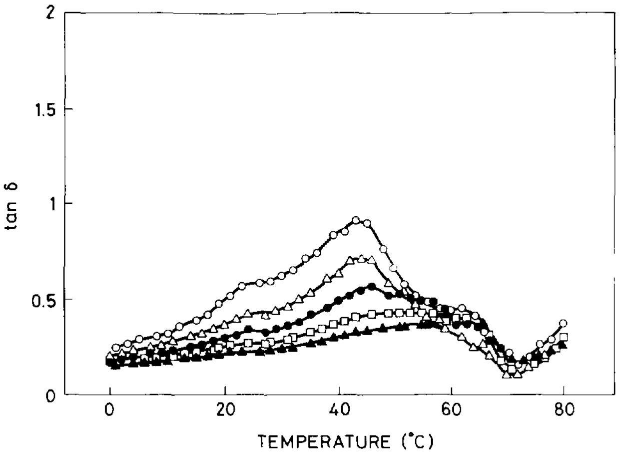

Figure 7 Temperature dependence of tan δ for LLDPE2 films measured at different frequencies: (○) 0.1; (△) 0.3; (●) 1; (□) 3; (▲) 10 Hz

The curves representing the dynamic mechanical results for the LLDPE films in terms of the loss tan δ in the α region, reported previously, only present a small shoulder and then they continuously increase as the temperature is increased[16]. This behaviour differs from that exhibited by the films used in this study (see *Figures 6* and *7*) where a close inspection of the loss tan δ *versus* T plots in the α region reveals the presence of two peaks, denoted, in increasing temperature order, by α

and α'', with the position of the second peak being somewhat different for the two LLDPE films; for example, the first peak for both films is centred at $\sim$30°C, whereas the second is centred at 50 and 80°C (at 3 Hz), for LLDPE2 and LLDPE1, respectively. The first peak is clearly related to the α relaxation process that appears in conventional polyethylene and therefore this is believed to be produced by motions of the chain folds at the crystal surface. It should be pointed out in this respect that although the α process occurs in the amorphous phase its development may require some mobility of the crystals. Studies carried out by Mandelkern and coworkers[23] have shown the T_α dependence on the thickness of the crystallites in such a way that T_α increases as the thickness increases. On the other hand, these studies suggest that more than a single α peak can be developed by control of crystallite thickness and distribution. According to this, the α' and α'' peaks in *Figures 6* and *7* may result from two groups of crystallites of slightly different thicknesses developed in the A and B layers. In support of this assumption it is necessary to point out that these well defined peaks are not detected in the relaxation spectrum corresponding to quenched strips obtained from moulded coextruded LLDPE films (*Figure 8*). It should be pointed out that a thorough study[24] carried out on the effect of the comonomer, i.e. octene, on the relaxation spectrum of LLDPE shows that the intensity of the α' peak is lowered by an increase in the comonomer content as a consequence of the decrease in crystallinity. The small difference in the location of the α' peak for LLDPE1 and LLDPE2 seems to suggest that motions in the chain folds at the surface of the crystals in each layer, and at the interphase of the AB coextruded layers, may play a major role in the development of this process.

The activation energies associated with the α' and α'' processes in the relaxation spectrum of LLDPE1 amount to 46.8±0.5 and 95±1 kcal mol^{-1}. While the activation energy for the α' relaxation of LLDPE2 could not be obtained from the experimental results, the value of this quantity obtained for the α'' process is 103±2 kcal mol^{-1}, which is close to the value found for this relaxation in the LLDPE1 films. It should be stressed that the value of the activation energy for the α' process in the LLDPE1 films is similar to that obtained by other workers[24] for the α relaxation. A close inspection of the storage relaxation modulus reveals an increase in E' in the α'' region which must be attributed to thickening of the crystals due to recrystallization processes. It is expected that as a consequence of the recrystallization the molecular motions in the interface will be hindered and hence the activation energy will be larger than that corresponding to the molecular motions in the α' process.

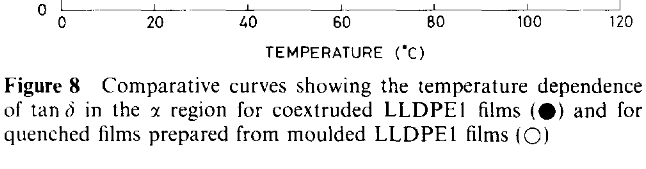

Figure 8 Comparative curves showing the temperature dependence of tan δ in the α region for coextruded LLDPE1 films (●) and for quenched films prepared from moulded LLDPE1 films (○)

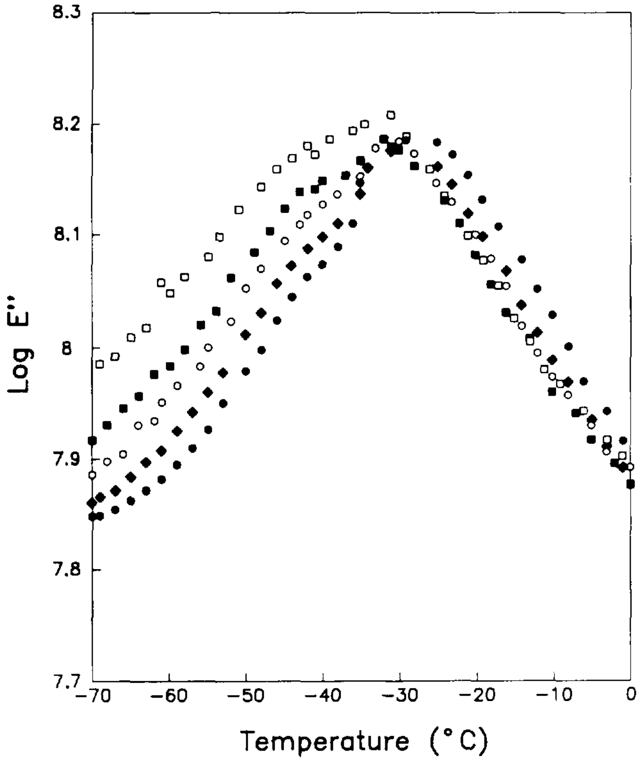

Figure 9 Temperature dependence of the loss relaxation modulus (in Pa) for LLDPE2 films in the β region measured at different frequencies: (□) 0.1; (■) 0.3; (○) 1; (◆) 3; (●) 10 Hz

Although the origin of the β relaxation process is still unresolved, it is commonly accepted that it is produced by motions taking place in the amorphous region[25]. Only a very small peak is detected in HDPE; the intensity of this peak, however, increases with the fraction of branching in the chains[26]. Moreover, as the branches are bulkier, the β relaxation shifts to higher temperatures[24]. These facts, in conjunction with the observation that the intensity of the β peak is higher in quenched polyethylene, led some authors to conclude that the β relaxation process is caused by generalized micro-Brownian motions in the amorphous phase and, as a consequence, it corresponds to a glass–rubber relaxation process[16,27]. The β relaxation in the coextruded LLDPE films studied in this work, as determined from the loss tan δ *versus* T plots, appears in the spectrum as an ostensible shoulder of the peak relating to the α relaxation process. However, as can be seen in *Figure 9*, the β relaxation appears as a well developed process when the viscoelastic results are expressed in terms of the relaxation loss modulus. This relaxation, in turn, seems to be the result of two overlapping peaks, centred at −36 and −30°C (at 1 Hz). The latter peak appears at the same temperature as that of the β relaxation process for strips moulded from the coextruded films. The location of the β relaxation process is not substantially affected by the microstructure of the latter films and therefore the motions that produce the process may occur in the amorphous phase. However, Mandelkern and coworkers[23] have shown that the intensity of the β transition is low for polyethylenes in which the interfacial content is much lower than 10%, but it increases rapidly as the interfacial content rises from 12 to 17%; hence, they concluded that the β relaxation process arises from motions taking place at the crystalline–amorphous interface. In view of these results one may safely conclude that both interfacial and amorphous regions are involved in the β process. The values of the activation energy corresponding to the second peak of the β relaxation process of the LLDPE1 and LLDPE2 films amount to 61.5 ± 0.5 and 60.9 ± 0.5 kcal mol^{-1}, respectively, which are only slightly lower than the values reported for the activation energy of the glass–rubber relaxation of most systems[25]. We must admit, however, that this value in itself is not sufficient evidence to identify the β relaxation process as the glass transition.

No significant changes are detected in the location and shape of the γ relaxation with respect to those reported for conventional LLDPE[16,24]. The intensity of the peak is similar to that reported for conventional branched polyethylenes and, therefore, lower than that of linear polyethylene of the same density. The activation energies obtained from the tan δ results were found to be ~18 and 20 kcal mol^{-1} for LLDPE1 and LLDPE2, respectively. This value is of the same order of magnitude as that theoretically estimated for crankshaft motions and hence it has been attributed to molecular motions involving three to four methylene groups in the amorphous phase, in addition to the reorientation of loose chain ends within the crystalline and amorphous fractions. The fact that the intensity of the relaxation is somewhat lower than that reported for most polyethylenes suggests that some tertiary carbons may disrupt the sequences of methylene groups in the amorphous phase which are necessary to produce the relaxation.

A close inspection of the results presented in *Figures 2* and *3*, where the temperature dependence of the diffusion coefficient on the temperature is depicted, shows two well differentiated regions, namely one where $T < 50°C$, in which the diffusion coefficient shows a moderate increase with temperature, followed by another region for $T > 50°C$ where a substantial increase in D with temperature is observed. These changes are shifted to slightly higher temperatures when oxygen is used as the permeant. The anomalous increase in the diffusion characteristics may not only be related to generalized motions involving amorphous segments and crystalline entities but in addition they may depend on the increase in solubility caused by melting of the less perfect crystalline entities. By comparing the permeability and the diffusion coefficients in *Figures 2* and *3* one can see that whereas the permeability coefficient at a given temperature is somewhat higher for LLDPE1 than for LLDPE2, the opposite occurs in the case of the diffusion coefficient. These results suggest, therefore, that the solubility of the permeant is higher in the former films than in the latter. However, the changes in solubility with temperature do not follow a definite path.

For homogeneous systems, the diffusion of gas occurs by a thermally activated process which satisfies the Arrhenius expression:

$$X = X_0 \exp(-E/RT) \qquad (7)$$

where X represents P or D, E becomes the activation energy of permeability E_P or the activation energy of diffusion E_D, and X_0 is a constant (P_0 or D_0), which is characteristic of the polymer–permeant system. The temperature dependence of the permeability can be expressed by two Arrhenius plots covering, respectively, the temperature intervals 20–50°C and 50–70°C. These plots for LLDPE1 and LLDPE2 are represented in *Figures 10* and *11*, respectively, with the values of the activation energies for O_2 and CO_2 being given in the third and fourth columns of *Table 1*. A significant decrease in the activation energy of the permeability can be detected in going from the low-temperature to the high-temperature interval, presumably as a consequence of the increase in solubility arising from initiation of the melting of the smaller crystalline entities, on the one hand, and to the increase in the molecular coiling of the oriented chains, on the other hand. The activation energy for the permeability in the 20–50°C interval is somewhat lower than that previously reported for highly oriented PE[10], presumably as a consequence of the relatively low crystallinity of the coextruded LLDPE films.

Similar Arrhenius plots over the temperature intervals indicated above also give a good representation of the temperature dependence of the diffusion coefficient. The values obtained for the apparent diffusion coefficient of the permeant are given in the fifth and sixth columns of *Table 1*. It is worth noting the relatively high activation energy exhibited by the apparent diffusion coefficient over the 50–70°C interval, compared to that obtained for the

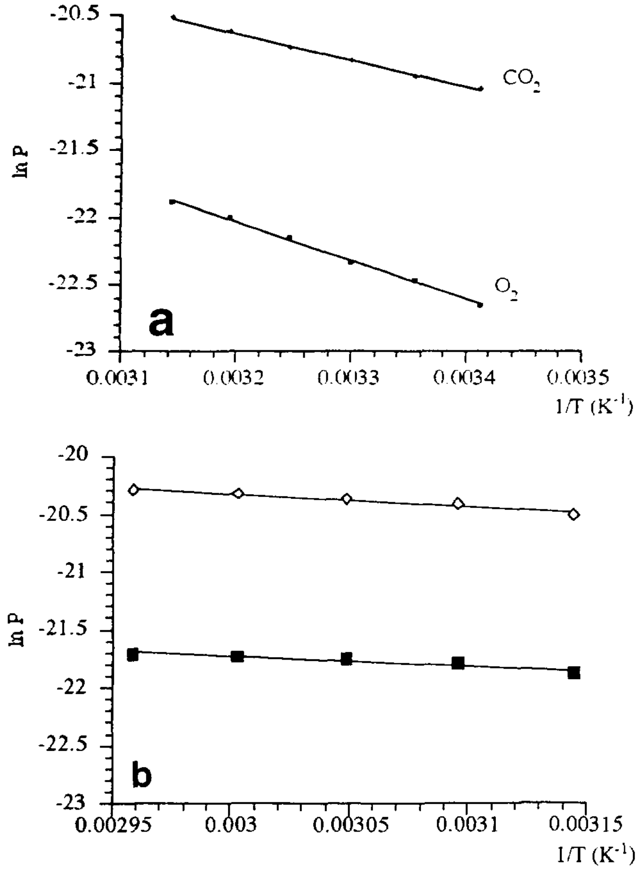

Figure 10 Arrhenius plots of the permeability coefficient (in barrers) of O_2 and CO_2 for LLDPE1 films over different temperature intervals: (a) 20–50°C (293–323 K); (b) 50–70°C (323–343 K)

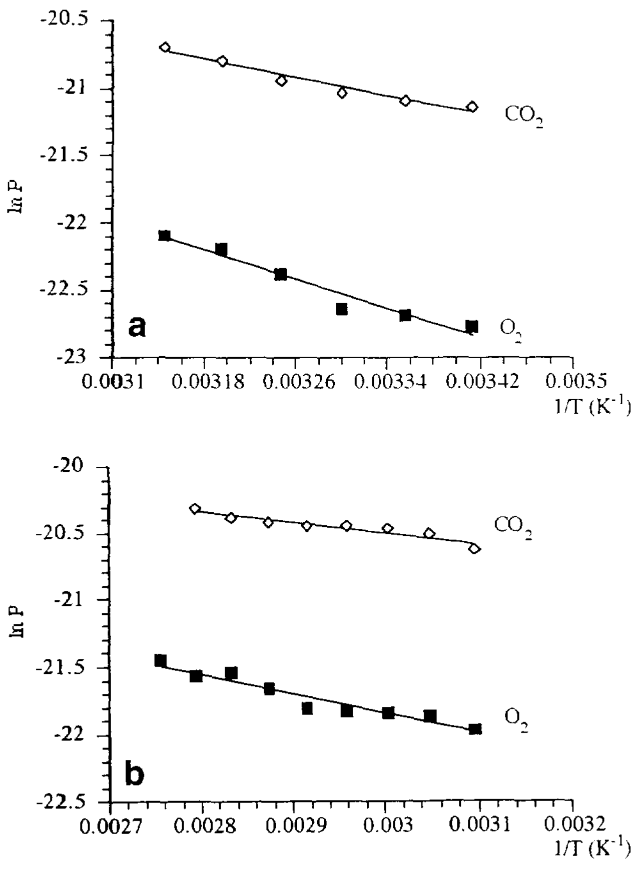

Figure 11 Arrhenius plots of the permeability coefficient (in barrers) of O_2 and CO_2 for LLDPE2 films over different temperature intervals: (a) 20–50°C (293–323 K); (b) 50–70°C (323–343 K)

Table 1 Activation energies for the permeability and diffusion of oxygen and carbon dioxide through LLDPE1 and LLDPE2 films

		E (kcal mol^{-1})			
		Permeability		Diffusion	
Film	Temperature interval (°C)	O_2	CO_2	O_2	CO_2
LLDPE1	20–45	5.8	3.9	3.0	2.5
LLDPE2	20–45	5.4	3.4	4.1	3.1
LLDPE1	50–70	1.8	2.3	9.4	12.9
LLDPE2	50–70	2.9	1.6	4.2	11.4

permeability over the same temperature interval. This behaviour suggests that gas diffusion through the films may not be a simple activated process, presumably as a consequence of the complicated motions that may take place in the α region, on the one hand, and to the morphological changes caused by recrystallization processes, on the other hand. Since the diffusion depends on the size of the diffusant molecules and on the structure of the polymer, it is useful to express the apparent diffusion coefficient in such a way that these factors are taken into consideration. Therefore, Michael and Parker[28] have expressed the apparent diffusion coefficient as follows:

$$D=\frac{D^*}{\tau\beta} \qquad (8)$$

where D^* is the diffusion coefficient for a completely amorphous polymer, τ is a geometric impedance factor that is related to the tortuosity of the path due to the presence of impermeable crystallites, and β is a chain immobilization factor that reflects the lack of mobility of segments in the crystalline–amorphous interphase and other contributing obstructive factors, such as the size of the permeant gas. According to this, the apparently high value of D in the 50–70°C interval may be mainly due to complicated changes in the mobility with temperature, which is accounted for by the parameter β. The substantial increase in the diffusion coefficient with temperature observed in the second region, in comparison with that of the first region, suggests that premelting processes, which presumably increase the free volume available for permeant jumping, overcome the reduction in free volume caused by recrystallization.

CONCLUSIONS

The relaxation spectra of coextruded LLDPE films, expressed in terms of loss tan δ, exhibit an α relaxation process which may be resolved into two peaks whose locations and intensities may be related to the motions of crystallite entities in the A and B layers. These peaks are not detected in the spectra corresponding to quenched strips moulded from the coextruded films. The β relaxation process, that appears as a shoulder of the α relaxation process in the tan δ *versus* T plots, becomes a well developed absorption when the results are expressed in terms of the loss relaxation modulus. No significant changes are detected in the location and shape of the γ relaxation with respect to those reported for conventional LLDPE.

The permeability and diffusion of gases through the films are not simple activated thermal processes. The diffusibility characteristics seem to be governed by molecular mobility, which in turn is affected by premelting and recrystallization processes occurring at temperatures above 50°C.

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