

Mechanical Relaxations and Diffusive Changes in Linear Low Density Polyethylene (LLDPE) Films Subject to Induced Stretching

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SYNOPSIS

An analysis of the diffusion of oxygen and carbon dioxide through linear low density polyethylene (LLDPE) subjected to longitudinal and transversal induced stretching in the ratio 2 : 1, is presented in this paper. The relaxation behavior of two coextruded LLDPE films prepared from copolymers of ethylene-1-octene is reported as well. The spectra, expressed in terms of loss $\tan \delta$, present a γ relaxation shifted 5°C to 10°C in the LLDPE1 with respect to the LLDPE2 when the stretching was longitudinal. This relaxation is lower in intensity than the one exhibited for conventional low-density polyethylene of the same crystallinity. Increasing the temperature order, a β relaxation process appears as an ostensible shoulder of the first of two relaxation processes, called α' and α'' , detected in the α region. The β relaxation, which is believed to be produced by motion taking place in the amorphous and interfacial regions, appears as two overlapping peaks centered at -36°C and -30°C for a longitudinal stretching and at -34°C and -28°C for a transversal stretching at 1 Hz. In relation to this fact, we observed a slight increase in the T_g of the LLDPE2 with respect to the LLDPE1, which is greater in the transversally stretched polymers than in the longitudinal ones. The values of the activation energy corresponding to the second peak of the β relaxation were obtained for the films subjected to stretching in longitudinal and transversal directions to the processing orientation. The study of the diffusional characteristics of oxygen and carbon dioxide through the films shows the temperature is related to the region for which the α processes are given. An anomalous behavior of the diffusion coefficient with the temperature is observed, suggesting general movements around the amorphous segments and crystalline entities. The increase with the temperature of both parameters (diffusion and permeability) can be attributed to a change in the gas solubility. This increase is greater for CO₂ than for O₂, which we interpret as a plastificant effect of the CO₂. Finally, the activation energies from diffusion coefficient and permeability are analyzed in terms of Arrhenius. The results show that the temperature dependence of the diffusive parameters may not be a simply activated process as a consequence of the fact that the diffusional characteristics of the films depend on their morphology which, in turn, is changing with temperature. Little changes are observed when the films are subjected to any kind of stretching. In this sense, we think that the orientation by tensile drawing will decrease the conformational entropy involved in melting processes and, as a consequence, will reduce both the permeability and the apparent diffusion coefficients. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

When small molecules permeate a polymer membrane, the rate of permeation can be expressed by parameters which may be characteristic of the poly-

mer. The study of gas diffusion through membranes has been developed by different investigators to determine selectivities, apparent diffusion coefficients, and permeability coefficients, but the mechanisms involved in the diffusional transport are poorly understood.¹⁻³

The penetrant diffusion's dependence on chain dynamics becomes clear if we consider that below the glass transition temperature (T_g), where the

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chains are frozen and only short-range motions are permitted, the value of the diffusion coefficient is severely reduced with respect to that of the diffusion coefficient above T_g .⁴

The permeation rate through polymer films is governed by the size of the permeating molecules and the dynamics of the molecular chains,^{5,6} being the last effect straightforwardly related to the structure of the chains. The effect of the chain dynamics on the diffusional characteristics of the films becomes especially clear if two regions are considered: below T_g and above it. In the first region, only short-range motions are allowed and the gas permeation is severely restricted. In the other region, above T_g , a great range of motions takes place. As a consequence, molecular chains with bulky side groups that hinder the conformational transitions about the backbone may exhibit relatively low diffusion characteristics, even at moderately high temperatures.⁷⁻¹¹

The microstructure of the films plays an important role in the diffusional process. In this sense, recent studies⁶ carried out on compression-molded films suggest that the mobility can be decreased and the transport may likely occur in a small volume fraction of a less-dense boundary phase. All this shows that the diffusional process is conditioned by the free volume and, therefore, sorption and diffusion take place almost exclusively through the amorphous regions.

The chemical structure also affects the microstructure of membranes, that is to say, 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 the film. 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 allowed to create holes through which the gas molecules randomly jump. The combination of a relatively low crystallinity and a moderate orientation is mainly responsible for their special physical characteristics.

Turning to the practical question, coextruded linear low density polyethylene films (LLDPE) show great commercial potential in the package industry due to their well-known good mechanical properties, specifically good processibility, increased stiffness in molded parts, and high resistance to tearing and toughness.

The purpose of this paper is to describe the change with the temperature of the apparent coefficients of permeability and diffusion of oxygen and carbon dioxide in coextruded LLDPE subjected to stretching, induced longitudinally and transversally, and to study their relation with the morphological

and structural changes observed from dynamic mechanical measurements. Although crystalline regions merely act as barriers impeding the flow, their effect in the permeation will also depend on the crystalline-amorphous interfaces which are influenced by the molecular orientation in the samples. In this sense we want to point out Holden and colleagues' thorough study¹⁰ on the effect of orientation on the gas permeability of LLDPE, which showed a large reduction of diffusion coefficient with increasing draw ratio (stretching in parallel and perpendicular directions to the processing orientation). We then observe that diffusion measurements provide a sensitive method of detecting structural changes, particularly in the non-crystalline region.

The aim of this paper is to relate the diffusion studies and relaxation processes to the morphology and structural changes observed when the LLDPE films are subjected to longitudinal and transversal stretching in the ratio 2 : 1. To achieve this purpose we have carried out dynamic mechanical analysis by DMTA in the longitudinal and transversal directions. Therefore, the mechanical relaxation spectra behavior of the LLDPE films subjected to stretching used in the gas transport measurements are analyzed, with special emphasis on the interpretation of the spectra in the interval of temperatures in which the diffusion studies were performed; with the intention of comparing the changes taking place in the analysis of longitudinal and transversal spectra. This correlation is important because it studies the diffusional characteristics of polymer films together with the influence of the orientation on the relaxation processes. Both processes are strongly dependent on the morphology of the films. For example, the development of the crystalline order reduces the solubility of the gas in the films while, on the other hand, it increases the tortuosity of the path followed by the diffusants in the matrix.

Studies by stretching, in polyurethanes, have already been analyzed by different investigators,¹²⁻¹⁴ but never for LLDPE following an electrochemical monitoring technique in the permeability and diffusion measurements.¹⁵⁻¹⁹ Therefore the temperature dependences of permeability and the diffusion coefficients of oxygen and carbon dioxide in LLDPE films, in parallel (stretched longitudinally) and perpendicular (stretched transversally) directions to the films' processing orientation, are studied here; the results are compared with those corresponding to undrawn films.

The viscoelastic studies of longitudinal and transversal stretching have been obtained in terms of the storage modulus E' , loss modulus E'' , and loss

$\tan \delta$ by DMTA measurements. The results are compared and discussed in terms of diffusion-observed measurements.

EXPERIMENTAL

Material

The LLDPE films used in this research were copolymers of ethylene-*co*-octene with ca. 8% of mol content of the last comonomer. Two LLDPE films were made up of three layers—A (15%), A (70%), B (15%)—in which the layers A and B were Dowlex/2247 ($\rho = 0.917 \text{ g/cm}^3$) and Dowlex/2291 ($\rho = 0.912 \text{ g/cm}^3$), respectively. The two films, LLDPE1 and LLDPE2, were obtained by coextrusion using the same raw materials but different processing conditions. The samples' thicknesses were about 25 μm for LLDPE1 and 23 μm for LLDPE2.

As a result of the processing conditions the films were oriented in the drawing direction and, as a consequence, they exhibit birefringence. This parameter was from $10^3 \times \Delta n$ to 1.4 and 2.86, for LLDPE1 and LLDPE2, respectively. The crystallinity degree of the films was determined from the melting endotherms; these values were 0.24 and 0.25 for LLDPE1 and LLDPE2, respectively. More details about these films will be given in another article, in preparation.

Dynamic Mechanical Measurements

The Storage relaxation modulus E' and loss $\tan \delta$ results for the two films were obtained from dynamic thermomechanical measurements with a PL-DMTA Mark-2 using the double cantilever inflexion method. The experiments were carried out at five different frequencies—0.1, 0.3, 1, 3, and 10 Hz—covering the temperature range from -140°C to 100°C at a heating rate of about $1^\circ\text{C}/\text{min}$. During the measurements the viscoelastometer applied a sinusoidal tensile strain at one edge of the sample; the sinusoidal tensile stress response was measured at the other side of the sample. In order to obtain information on how the orientation affects the dynamic-mechanical behavior of the films, the samples were placed in the viscoelastometer longitudinally (in parallel) and transversally (perpendicular) to the processing orientation, depending on the study. The value of the complex dynamic tensile modulus could be calculated from the dynamic force, whereas the tangent of the phase angle δ between the stress and strain was read directly from the instrument. Changes of real E' and imaginary E'' parts of the

complex dynamic tensile modulus E and $\tan \delta$, with the temperature, were obtained for each sample and direction.

Apparent Permeability and Diffusion Coefficient Measurements

The oxygen and carbon dioxide permeabilities through LLDPE were determined by an electrochemical monitoring technique. The permeation cell used in this paper is based on the experimental set-up generally used by other researchers. More detailed explanations about the experimental procedure can be found elsewhere.¹⁵⁻²¹

The electrochemical technique for obtaining the oxygen permeability is based on the Clark oxygen electrode and has been applied previously by different researchers. This technique has also been used to measure the apparent permeability coefficients of dissolved carbon dioxide by applying an electrode sensor (model 95-02 of the Orion Research Incorporated Laboratory) in a liquid-liquid diffusion cell similar to the oxygen sensor cell,^{15,16,19} combined with a pH meter.¹⁷

The oxygen sensor based on the Clark oxygen electrode measures the electrical current resulting from the cathodic reaction



The apparent permeability coefficient is then given by^{15,16}

$$P = Dk = \frac{I(t \rightarrow \infty) \cdot L}{\nu \cdot F \cdot A \cdot \Delta p} \quad (2)$$

where D is the diffusion coefficient, k the solubility coefficient, I is the current intensity in the steady state, ν is the number of electrons transferred in the cathodic reaction ($\nu = 4$), F is Faraday's constant ($F = 96500 \text{ C mol}^{-1}$), L is the polymer film thickness, A is the effective area of the membrane (the same as the sensor surface, $(14.24 \pm 0.13) 10^{-2} \text{ cm}^2$) and $\Delta p = 155 \pm 1 \text{ mm of Hg}$.

The permeability of carbon dioxide was measured by using a cell made of Pyrex glass designed especially for permeability measurements similar to the ones used by Nakagawa and coworkers.¹⁷ The sensor fitted to the cell was an Orion 95-02 which determines the amount of CO_2 as follows: carbon dioxide that permeated through a membrane from the downstream side is dissolved and reaches equilibrium in the solution placed upstream where the sensor is situated. The reaction produced is

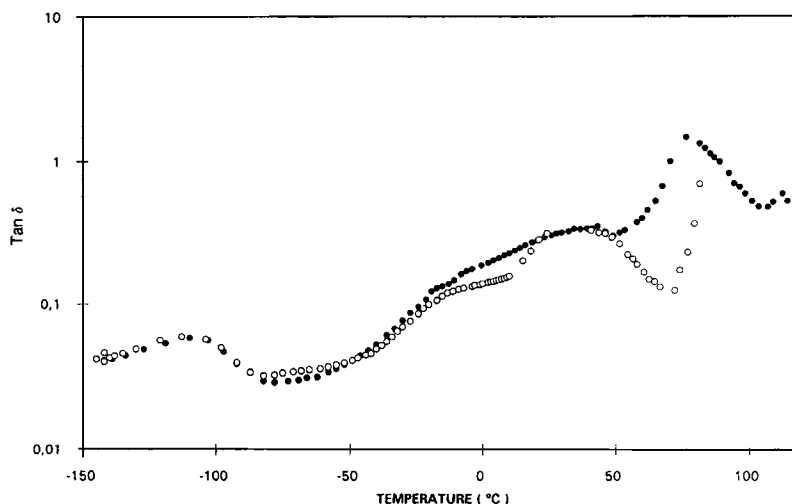


Figure 1 Changes with temperature in the loss relaxation modulus in Pa for strips of stuck LLDPE1 films stretched longitudinally (●) and transversally (○).



If we follow the procedure described by Nakagawa and colleagues,¹⁷ the apparent permeability coefficient, P , can be obtained by the equation

$$P = L \left(\frac{dc}{dt} \right) V \left[A \left(p_0 - \frac{c_1}{\alpha} \right) \right] \quad (4)$$

where V is the cell volume at the downstream side, about 150 cm³; L is the thickness of sample; A is the effective area of the membrane (about 4.15 ± 0.05 cm²); p_0 is the CO₂ partial pressure at the upstream side (about 76 cm of Hg); α is the Bunsen constant (we have taken 0.759 cm Hg⁻¹); and c_1 is the carbon dioxide concentration, i.e., the H⁺ concentration obtained from the pH measurement. More details about the experimental conditions and calibration cell can be found in the reference mentioned above.¹⁷

RESULTS AND DISCUSSION

It is widely known that high-, low-, and linear low-density polyethylene—usually represented as HDPE, LDPE, and LLDPE, respectively—present three main relaxations extending from -120°C to -70°C (γ), from -70°C to 10°C (β), and from 10°C to 50°C (α),²²⁻²⁷ approximately.

The T_α temperature, at which the maximum peak appears, is placed for the LLDPE at approx. 30°C , so this peak is placed between the HDPE peak (approx. 52°C) and the LDPE peak (approx. 18°C). As is widely known, the intensity of the α absorption in HDPE is significantly greater than the intensity

of LDPE, which suggests to us that the α peak is representative of the crystalline phase and consequently is originated from different kinds of movements in the crystal at the interface areas rather than movements at the amorphous phase.²⁸⁻³⁰

Generally, the plots showing the dynamic-mechanical results for LLDPE films in terms of the loss $\tan \delta$ in the α region present only a small shoulder, after which they increase as the temperature continuously rises.²³ Nevertheless, this behavior differs from the behavior checked in the present paper, where a close inspection of the loss $\tan \delta$ versus T reveals the presence of two peaks named, by increasing temperature, α' and α'' (Figs. 1 and 2). While the first peak is centered ca. 30 – 40°C in both films (LLDPE1 and LLDPE2), the second one is situated at 50°C and 80°C , at 3 Hz, for LLDPE2 and LLDPE1, respectively, when the films are stretched longitudinally. These maximums however, somewhat displaced forward greater temperatures when the polyethylenes were transversally stretched (Figs. 3 and 4).

It should be emphasized that when the polymers are subjected to a transversal stretching the evolution of $\tan \delta$ versus T is very different from the evolution that occurs with longitudinal stretching. On the other hand, $\tan \delta$ is greater for LLDPE1 than for LLDPE2 in the γ region, although this behavior is reversed in the β and α regions. The α region is subdivided into two peaks, α' and α'' (See Figs. 3 and 4 for LLDPE1 and LLDPE2 α regions subjected to transversal and longitudinal stretching, respectively.) Otherwise, these peaks are stronger in the LLDPE2 than in the LLDPE1, and they have more intensity and are stronger in the transversal

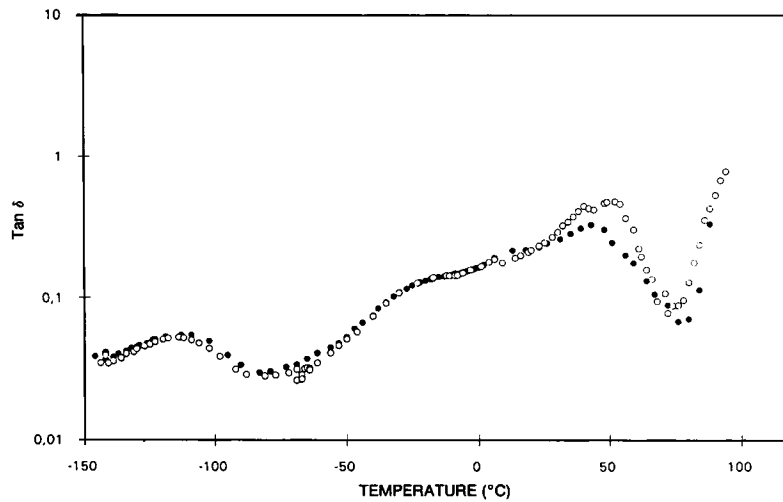


Figure 2 Changes with temperature in the loss relaxation modulus in Pa for strips of stuck LLDPE2 films stretched longitudinally (●) and transversally (○).

stretching than in the longitudinal. This relaxation process was attributed to crystallite thickening. Actually, longitudinal stretching not only favors further orientation at the amorphous-crystalline interface but also causes a decrease in the free energy of crystallization at the interface along that direction of stretching which favors crystallite thickening. On the other hand, transversal stretching may make the crystallites more spherical, thus disrupting some of the interfacial orientation and reducing the

thickening of the crystallites. Consequently, the fact that the α -peak is more pronounced in the transversally stretched films than in the longitudinally stretched ones suggests that the peaks are produced by motions taking place in the crystalline-amorphous interface.

The first peak is clearly related to the α relaxation process which takes place in the conventional polyethylenes; in our opinion, this fact can be due to motions of the chain folds on the crystal surface. It

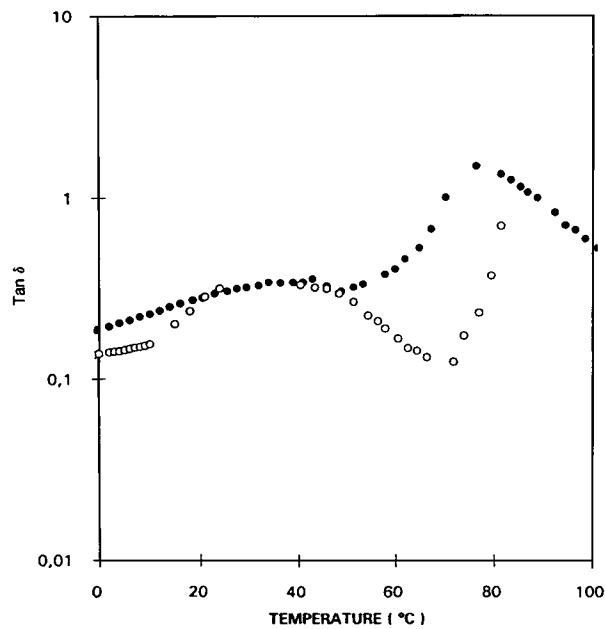


Figure 3 Temperature-related changes in α region of the loss relaxation modulus in Pa for strips of stuck LLDPE1 films stretched longitudinally (●) and transversally (○).

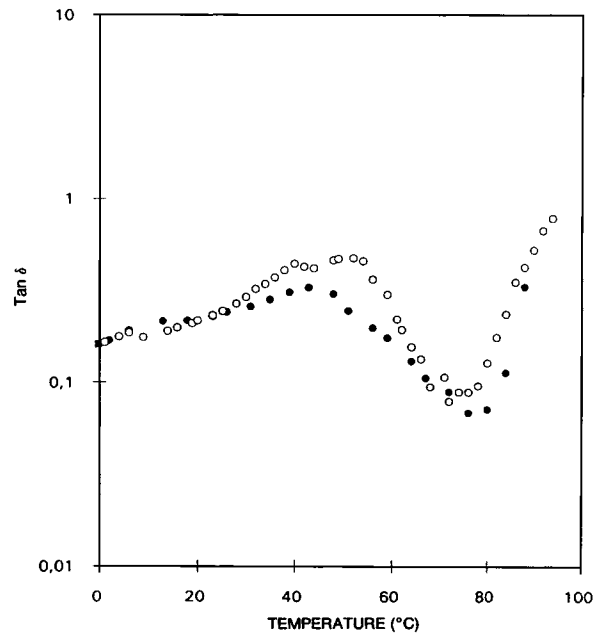


Figure 4 Temperature-related changes in α region of the loss relaxation modulus in Pa for strips of stuck LLDPE2 films stretched longitudinally (●) and transversally (○).

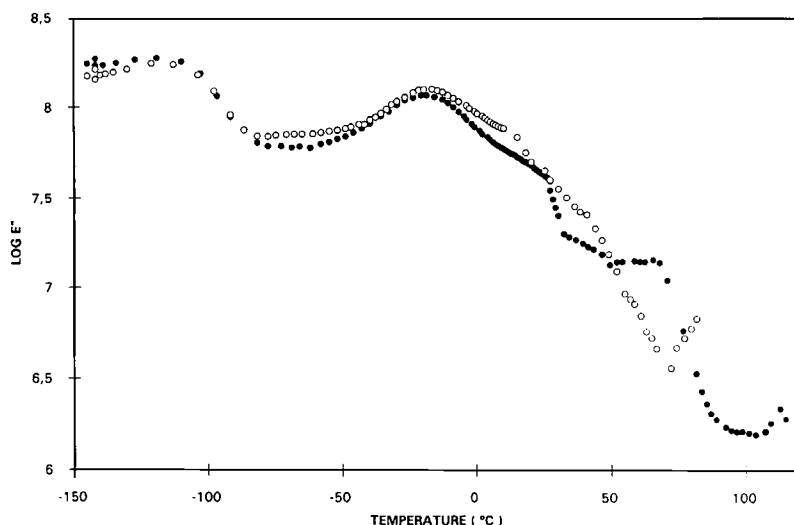


Figure 5 Temperature dependence of the storage relaxation modulus in Pa for strips of stuck LLDPE1 films subjected to stretching longitudinally (●) and transversally (○).

should be said that when the α process occurs in the amorphous phase, its development may require mobility of the crystals. This mobility is increased with transversal rather than longitudinal stretching. On the other hand, it could be thought that the two peaks into which the α region is subdivided, α' and α'' , (Figs. 3 and 4), could be due to two kinds of crystals with slightly different thickness developed in layers A and B.

It should also be pointed out that a thorough study (Clas and colleagues³¹) of the comonomer octene effect on the relaxation spectrum of LLDPE shows that the intensity of the α' peak is lowered by an increase of the comonomer content as a consequence of the decrease in crystallinity.

The small difference between the locations of the α' peaks for LLDPE1 and LLDPE2 longitudinally and transversally stretched suggests that the motion in the chain folds on the crystals surface in each layer and at the interphase of the AB coextruded layers may play a role in the development of this process. The transversal stretching (perpendicular to the processing orientation) could favor an increased crystallinity at the same temperature. Furthermore, the copolymer presence could help increase the crystal mobilities.

Studies carried out by Mandelkern and coworkers,³⁰ have pointed out that the T_α increases with the sample thickness. In relation to this fact, we observed in our study a slight increase in the T_α of the LLDPE2 with respect to the LLDPE1, which is greater in the transversally stretched polymers than in those longitudinally stretched. R. M. Gohil³² has found a useful relationship for predicting oxygen

permeability for biaxially oriented PET films prepared under a variety of processing conditions.

Figures 5 and 6 show the variation of $\log E''$ versus T for LLDPE1 and LLDPE2 subjected to longitudinal and transversal stretching. We can see that the curves are quite similar for both films as far as the relaxation of α , where the above-mentioned changes appear; unlike the values of the loss modulus for LLDPE1 and LLDPE2, which were slightly different when the films were subjected to longitudinal rather than transversal stretching. We think this is one indication about the orientation which has no noticeable influence on these processes.

It is commonly known that in the β region, the relaxation processes are produced by movements around the amorphous zone.³²⁻³⁵ These movements are usually microbrownians as a consequence of the relaxation process between glass and rubber phases.^{23,33,36-38}

As in the case of the α relaxation, the β relaxation in co-extruded LLDPE films, transversally and longitudinally stretched, is obtained from the spectrum in which it appears as an ostensible shoulder of the α relaxation process. The results show two overlapping peaks centered at -36°C and -30°C for longitudinal stretching and at -34°C and -28°C for transversal stretching, at 1 Hz.

The values of the activation energy corresponding to the second peak of the β relaxation of LLDPE1 and LLDPE2 subjected to longitudinal stretching are 61.5 ± 0.5 kcal/mol and 60.9 ± 0.5 kcal/mol, respectively. On the other hand, for LLDPE1 and LLDPE2 subjected to transversal stretching the results are 65.2 ± 0.5 and 63.4 ± 0.5 Kcal/mol, re-

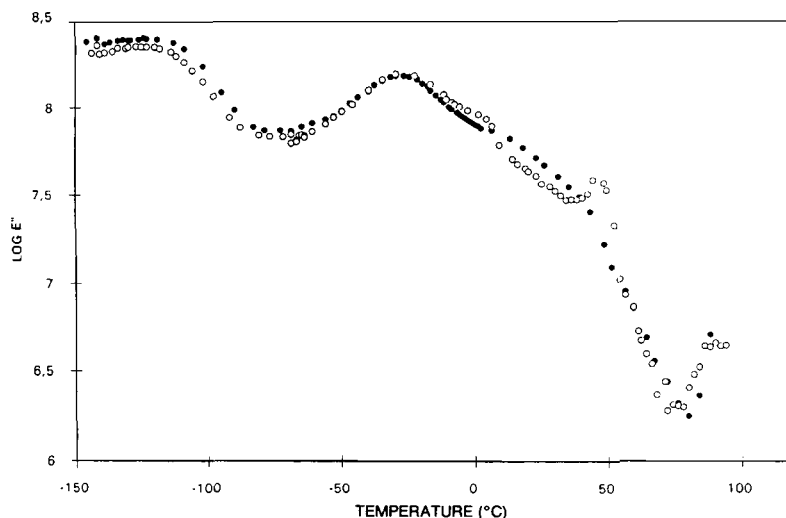


Figure 6 Temperature dependence of the storage relaxation modulus in Pa for strips of stuck LLDPE2 films subjected to stretching longitudinally (●) and transversally (○).

spectively. These values have been obtained from Figures 7, 8, 9, and 10, studying the relationship between the frequency and the temperature, which shows an Arrhenius dependence:

$$\nu = \nu_0 \exp(-E/RT) \quad (5)$$

where R is the universal gas constant, E is the apparent activation energy, and ν_0 is a constant depending on the system.

The values of this research are not very different from the values reported in the bibliography for the activation energy at the glass-rubber relaxation of

most systems,³³⁻³⁵ although they are different when the polymers have been subjected to different treatments in their manufacture. We must admit, however, that these values alone are not enough to identify the relaxation β process as the glass transition.

To finish our thermomechanical analysis we now address the γ relaxation. No significant changes have been found in the location and shape of the γ relaxation from the one reported in the bibliography. However, we have observed a slight displacement of 5°C to 10°C in the LLDPE1 with respect to the LLDPE2 where the films are subjected to longitudinal stretching. The opposite is true in the trans-

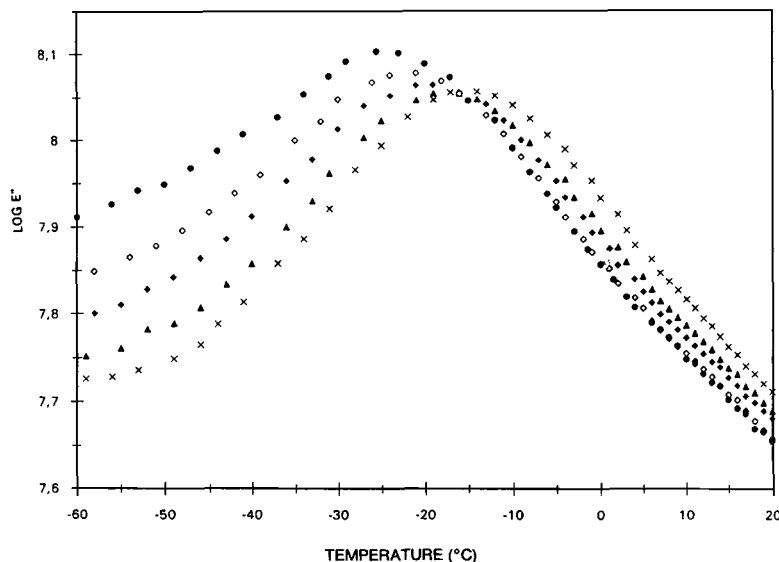


Figure 7 Temperature dependence of the storage relaxation modulus in Pa for LLDPE1 films stretched longitudinally in the β region at several frequencies: (●) 0.1, (◇) 0.3, (◆) 1, (▲) 3, and (×) 10 Hz.

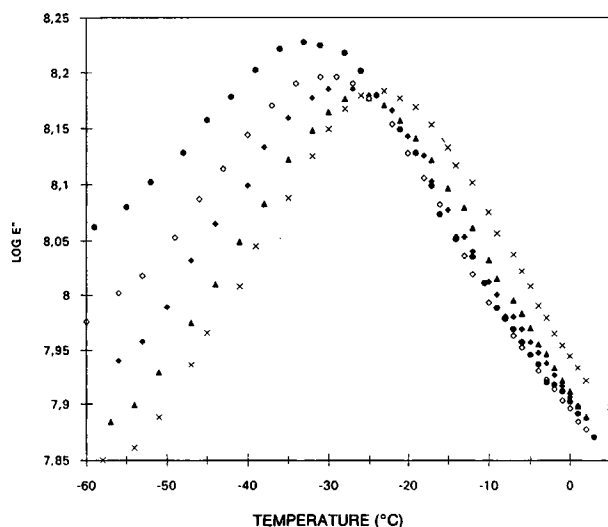


Figure 8 Temperature dependence of the storage relaxation modulus in Pa for LLDPE2 films stretched longitudinally in the β region at several frequencies: (●) 0.1, (◇) 0.3, (◆) 1, (▲) 3, and (×) 10 Hz.

versal stretching, where the $\tan \delta$ is slightly greater in LLDPE1 than LLDPE2. The same thing happens when we analyze the plot $\log E''$ versus T .

As for activation energies of the γ relaxation, these values can be obtained from the $\tan \delta$; the results were 18 and 20 kcal/mol for the LLDPE1 and LLDPE2, respectively, when the films were subjected to longitudinal stretching and 20 and 22 kcal/mol when they were transversally stretched. These values have the same order of magnitude as those theoretically estimated for crankshaft motions and hence, they have been attributed to molecular motions involving three to four methylene groups in the amorphous phase, as well as 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 must disrupt the sequences of methylene groups in the amorphous phase necessary to produce the relaxation.

The next step in our dissertation will be the analysis of the diffusion and permeability results obtained by electrochemical monitoring sensor.

Experiments up to 50°C cannot be performed by the method mentioned above due to its inconvenience. Thus the diffusion and permeability studies (for O_2 and CO_2) have been carried out in the region of α relaxation processes; that is, from 20°C to 50°C. In spite of this fact and due to the interest in studying the effect of stretching in temperatures above 50°C (that is, at $T > T_{\alpha'}$), we will try to achieve this

purpose by employing the pressure method instead of the electrochemical method.

Figures 11 and 12 show temperature dependence of the apparent permeability coefficient, P , through LLDPE1 and LLDPE2 films. We observed a similar shape and evolution of the curves for both stretching directions and for both polyethylenes, although the values of oxygen permeability are smaller than the values corresponding to carbon dioxide.

The apparent diffusion coefficients for O_2 and CO_2 through LLDPE1 and LLDPE2 films have been obtained from time-lag method, $D = L^2/6\tau$, where D is the diffusion coefficient, L is the thickness of sample and τ is the time lag.¹⁵ The results are plotted as functions of the temperature in Figures 13 and 14. It should be noted that the permeability at a fixed temperature is greater in the LLDPE1 than in the LLDPE2, whereas the diffusion coefficient is greater in the LLDPE2. This difference is stronger in the oxygen and in the region of temperatures above $T_{\alpha'}$.

A close inspection of the plots D versus T , which depict the dependence of the parameter on the temperature, shows two well-differentiated regions (for both films and for both stretchings): one region at $T < T_{\alpha'}$ where the diffusion coefficient increases moderately with the temperature; and another region ($T > T_{\alpha'}$) in which a substantial increase in D (and also in P) is observed.

The anomalous behavior of the diffusion coefficient with the temperature suggests to us that these changes can be related to general movements around the amorphous segments and crystalline entities. Moreover, some tertiary carbons may disrupt the sequences of methylene groups in the amorphous phase which are necessary to produce the relaxation. The increase with temperature in both parameters (diffusion coefficient and permeability) can be attributed to a change in the gas solubility. This increase is greater in the CO_2 than in the O_2 , which suggests to us a plastificant effect of the CO_2 , as has been shown by other researchers³⁹⁻⁴¹; and also suggests that this increase in solubility arises from initiation of the melting of the smaller crystalline entities and from the increase in the molecular coiling of the oriented chains.

Turning to the stretching question, we see a slight decrease in the permeability for both stretchings; this decrease is much stronger for CO_2 than for O_2 . However, even in the LLDPE1 film (Fig. 11), a significant difference in the permeability for the two stretchings, longitudinal and transversal, is seen only above 40°C. In the LLDPE2 film (Fig. 12) the differences are much less significant at any temperature. We think that the orientation by tensile

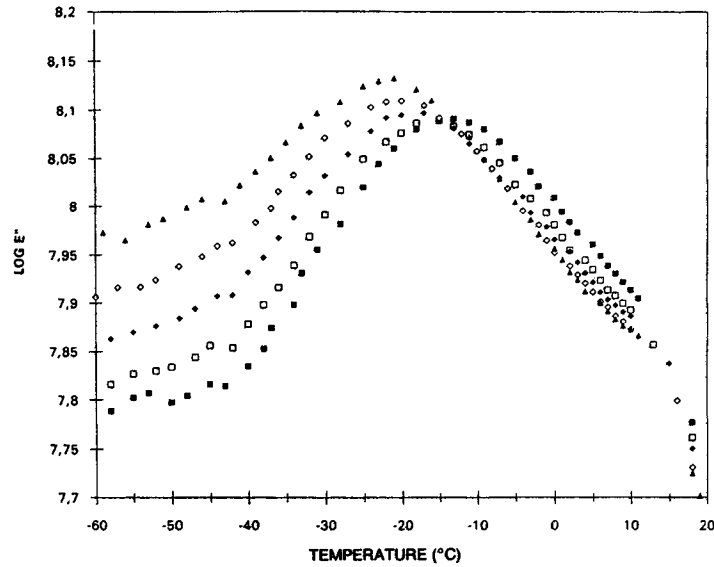


Figure 9 Temperature dependence of the storage relaxation modulus in Pa for LLDPE1 films stretched transversally in the β region at several frequencies: (\blacktriangle) 0.1, (\diamond) 0.3, (\bullet) 1, (\square) 3, and (\blacksquare) 10 Hz.

drawing will decrease the conformational entropy involved in the melting process and, as a consequence, the melting of small crystalline entities will be shifted to higher temperatures, thus reducing both the permeability and the apparent diffusion coefficients. The reductions observed in drawing are consistent with earlier results reported by Holden and coworkers¹⁰ for highly oriented polyethylene. Based on works carried out by several investigators, Holden and colleagues attribute this reduction to the fact that on drawing, the initial spherulitic structure

transforms into a new microfibrillar structure. It has been postulated that microshear processes on the surface of the fibrils may produce extended molecules and also the possibility of some crystal thickening. This physical picture, which explains Holden and coworkers' results, could also account for the results reported in this paper.

If we compare the temperature dependence of both the apparent permeability and the diffusion (Figs. 11–14), we observe that the changes are greater when the polymers have been subjected to

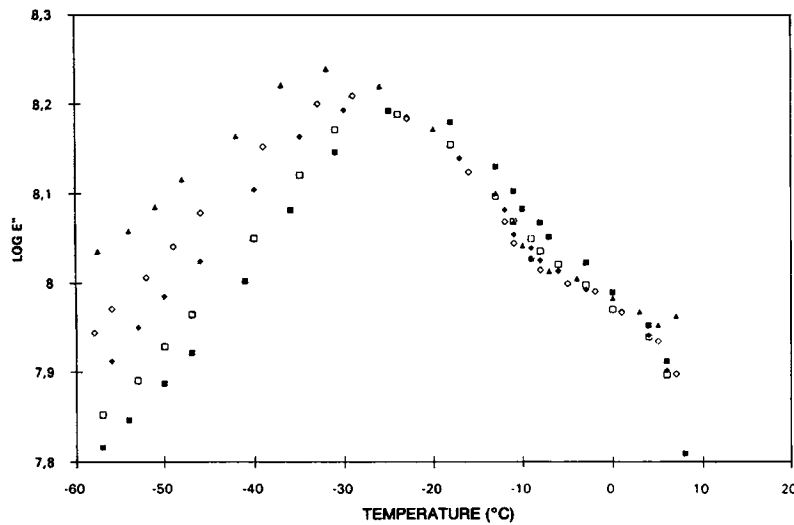


Figure 10 Temperature dependence of the storage relaxation modulus in Pa for LLDPE2 films stretched transversally in the β region at several frequencies: (\blacktriangle) 0.1, (\diamond) 0.3, (\bullet) 1, (\square) 3, and (\blacksquare) 10 Hz.

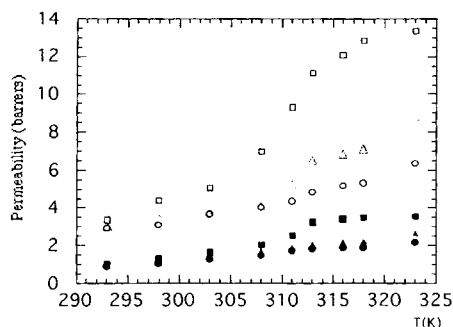


Figure 11 Temperature dependence of the apparent permeability coefficient of O_2 and CO_2 through LLDPE1 film: (a) without stretching (\blacksquare for O_2 and \square for CO_2); (b) stretched longitudinally (\bullet for O_2 and \circ for CO_2); (c) stretched transversally (\blacktriangle for O_2 and \triangle for CO_2).

a transversal rather than longitudinal stretching. In both cases, however, this dependence is lower than in the unstretched films. That effect could be due to the fact that the small crystals formed in the amorphous zone have less volume; consequently the gas solubility in the polymer increases and so does the permeability. The apparent permeability for a given temperature is bigger in the LLDPE1 than LLDPE2; the opposite is true for the diffusion coefficient. The fact that the changes in the diffusion and in the permeability are much greater than in the high temperature region might be due to the melting of small crystalline entities. On the other hand, this melting might increase the solubility of the gases in the films, increasing the permeabilities and decreasing the tortuosity path factor and favoring the diffusion process. If we think of an unstretched film, the crystallites might be spherical (spherulites). Rolling this film out and stretching the film thickens the crystallites in the direction perpendicular to the stretching, making prolate el-

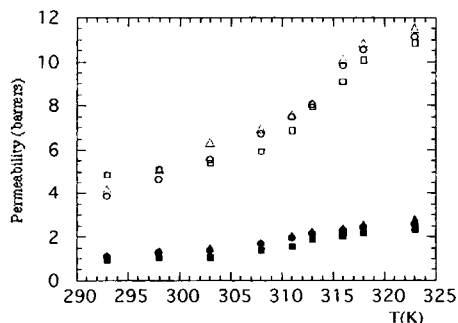


Figure 12 Temperature dependence of the apparent permeability coefficient of O_2 and CO_2 through LLDPE2 film: (a) without stretching (\blacksquare for O_2 and \square for CO_2); (b) stretched longitudinally (\bullet for O_2 and \circ for CO_2); (c) stretched transversally (\blacktriangle for O_2 and \triangle for CO_2).

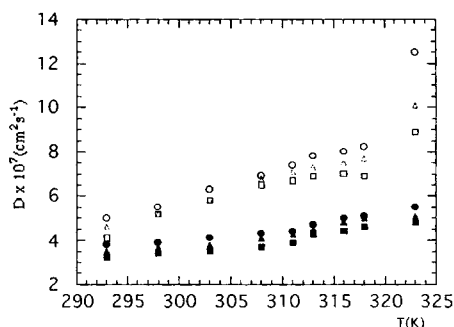


Figure 13 Variation in the diffusion coefficients of O_2 and CO_2 through LLDPE1 film: (a) without stretching (\blacktriangle for O_2 and \triangle for CO_2); (b) stretched longitudinally (\blacksquare for O_2 and \square for CO_2); (c) stretched transversally (\bullet for O_2 and \circ for CO_2).

lipoids, for example. A further stretching in this direction (longitudinal stretching) prolongs the perpendicularly oriented ellipsoids. On the other hand, stretching in the other direction again promotes an approach to the initial situation with spherulites (transverse stretching). In the latter case, the tortuosity of the diffusion path is reduced compared to the former case, and therefore the D_T is greater than D_L . The diffusion coefficient in the original film (without stretching) should be in between those values. This is indeed observed in both polymers and for all gases studied. These facts support the tortuosity explanation presented here.

As we have mentioned above, the polymer's change in behavior occurs 5 degrees earlier if O_2 is employed as permeant. This difference is more evident when the temperature is $T > T_{\alpha'}$.

To finish, we will discuss the activation energies obtained. In order to calculate these energies we have studied the Arrhenius plots in the range of temperatures from 293–321 K. In this paper we have ad-

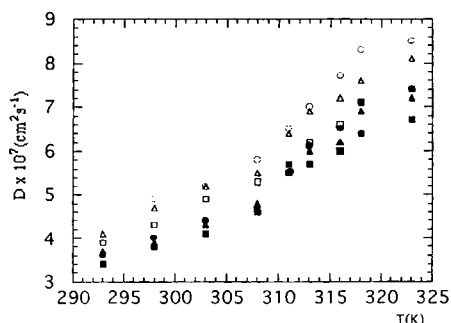


Figure 14 Variation in the diffusion coefficients of O_2 and CO_2 through LLDPE2 film: (a) without stretching (\blacktriangle for O_2 and \triangle for CO_2); (b) stretched longitudinally (\blacksquare for O_2 and \square for CO_2); (c) stretched transversally (\bullet for O_2 and \circ for CO_2).

Table I Activation Energies in kcal/mol for the Oxygen and Carbon Dioxide Obtained from Permeabilities and Diffusion Coefficient Measurements through LLDPE1 and LLDPE2

Film	T (interval)	Permeability						Diffusion					
		Oxygen			Carbon Dioxide			Oxygen			Carbon Dioxide		
		N ^a	SL ^b	ST ^c	N ^a	SL ^b	ST ^c	N ^a	SL ^b	ST ^c	N ^a	SL ^b	ST ^c
LLDPE1	20–50°C	9.8	6.5	7.3	10.6	5.0	7.0	2.6	2.7	2.4	4.4	4.0	4.8
LLDPE2	20–50°C	6.6	5.0	5.8	7.1	5.6	6.6	4.6	4.6	5.0	4.4	4.2	4.5

^a Undrawn film.

^b Longitudinal stretching induced; ratio, 2 : 1.

^c Transversal stretching induced; ratio, 2 : 1.

mitted that a thermally activated process follows the Arrhenius equation:

$$X = X_0 \exp(E_x/RT) \quad (6)$$

where X can be both P or D ; E_x is the activation energy (E_p for the permeability and E_D for the diffusion) and X_0 is a constant that depends on the system formed by the polymer and the penetrant molecule.

The activation energies collected in Table I have been obtained by the slope of the straight line of the $\ln X$ versus $1/T$.

First, we will analyze the results obtained from the permeability. We can see a small decrease of the E_p in the LLDPE2 with respect to the LLDPE1, and another decrease when the polymer is subjected to any kind of stretching (slightly lower in the case of longitudinal than in transversal stretching). This decrease can be assigned not only to an increase in the solubility arising from the melting start of the smallest crystalline entities but also to an increase in the molecular coiling of the oriented chains. The observed activation energy, E_p , is slightly lower than in the case of highly oriented polyethylenes in this range of temperatures,¹⁰ which can be understood as a consequence of the low crystallinity of the LLDPE films.

Thus, when we examine the diffusion activation energies, E_D , in the same table, we can find only slight changes among the different states of the studied polymer. Moreover, in contrast to the behavior of E_p , the E_D values in LLDPE1 films are smaller than in LLDPE2 and show a slight increase in the longitudinal stretching with respect to the two other cases.

This behavior suggest to us that it is likely due to complicated movements, which can take place as a consequence of the diffusion of molecules through the polymer, brownian movements that may appear

in the zone and may yield morphological changes caused by the recrystallization processes. Furthermore, these changes are different when the polymer is subjected to different types of stretching: greater for CO₂ than for O₂ in the LLDPE1, and quite similar in the LLDPE2.

Finally, from the experimental results of permeability and diffusion coefficient given in Figures 11–14, we suggest that the temperature dependence of the diffusive parameters may not be a simply activated process as a consequence of the fact that the diffusional characteristics of the films depend on their morphology which, in turn, is changing with temperature.

This research was supported by the DGICYT (Dirección General de Investigación en Ciencia y Tecnología) and the EC through the project PB92-0773-C03-03 and BRITE-EURAM-BE-PROJECT 4104.

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Received May 26, 1995

Accepted November 1, 1995