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# Thermomechanical and diffusive studies in films prepared from copolymers of ethylene-1-octene subject to longitudinal and transversal induced stretching

**J. P. García-Villaluenga* and B. Seoane**
*Departamento de Física Aplicada I, Facultad de Física, UCM, 28040 Madrid, Spain*

**and V. Compañ**
*Departamento de Física, Universidad Jaime I, 12080 Castellón, Spain*

**and R. Díaz-Calleja**
*Departamento de Termodinámica Aplicada, UPV, 46022 Valencia, Spain*
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The effects of induced stretching on the relaxation behaviour and on gas transport properties in coextruded linear low-density polyethylene (LLDPE) films, prepared from copolymers of ethylene-1-octene, are reported. The spectra show that the stretching, regardless of the direction of its application, does not produce significant changes in the $\gamma$ and $\beta$ relaxation processes. However, in the $\alpha$ region, there are some differences in the relaxation response depending on the direction of the induced stretching. The longitudinal stretching gives rise to a displacement of the temperature at which the $\alpha''$ process occurs in LLDPE2 film with respect to LLDPE1 film. On the other hand, the transverse stretching does not produce a displacement of the $\alpha''$ relaxation, but it does produce a decrease of intensity of the $\alpha'$ relaxation peak in both films. Transport coefficients have been measured for $CO_2$ and $O_2$ in stretched polyethylene samples over temperatures ranging from 25 to 85°C. In all cases, a linear plot of the logarithm of the gas transport coefficients as a function of the reciprocal absolute temperature is observed, indicating that activated diffusion is occurring. Similarly, a break in these Arrhenius plots can be noted at nearly the same temperature range as reported in the thermomechanical study. The activation energies associated with the transport mechanism are reported. On the other hand, the results reveal that the films are dependent on thermal history. In order to obtain reproducible results, a suitable control of the thermal conditioning of the films is advisable. © 1997 Elsevier Science Ltd.

**(Keywords: LLDPE films; stretching; mechanical relaxation)**

## INTRODUCTION

Linear low-density polyethylene (LLDPE) has been a great commercial success in the area of food and beverage packaging. It seems that the combination of a relatively low crystallinity and a moderate orientation are mainly responsible for its special physical characteristics. Some of the advantages of these special properties, such as high tear strength and toughness in films, improved environmental stress cracking resistance, and good processability and increased stiffness in moulded parts, have contributed to an increase in its application range. Likewise, our interest in stressed polymers stemmed from experimental work spanning recent years in which some polymers were stretched to monitor the infrared or Raman spectra[1,2], to study the rheological and mechanical characteristics[3], to examine the mechanism of gas transport in polymeric films[4], or to test previous theoretical studies[5,6].

In a previous work[7], the mechanical relaxation and the diffusional characteristics of the coextruded LLDPE films, prepared from copolymers of ethylene-1-octene, were reported. The spectra presented a $\gamma$ relaxation of lower intensity than that exhibited by conventional low-density polyethylene of the same crystallinity, followed, with increasing temperature, by a $\beta$ relaxation process that appeared as a shoulder of the first of two relaxation processes, denoted by $\alpha'$ and $\alpha''$, detected in the $\alpha$ region.

In the present work, we have studied the change with temperature of the permeability, diffusion and solubility coefficients of oxygen and carbon dioxide in coextruded LLDPE subject to longitudinal and transverse stretching, in order to relate the effects of both kinds of stretching to the transport parameters. On the other hand, the induced stretching in the films could modify their mechanical and diffusive properties. In this way, we try to relate the diffusion studies to the morphological and structural changes observed when the LLDPE is subject to longitudinal and transverse stretching in the ratio 2:1. We have carried out a dynamic mechanical

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* To whom correspondence should be addressed

analysis by dynamic mechanical thermal analysis (d.m.t.a.) in the longitudinal and transverse direction. Therefore, the mechanical relaxation spectra behaviour of the LLDPE films subject to stretching used in the gas transport measurements is analysed, giving special emphasis to the interpretation of the spectra in the interval of temperatures in which the diffusion studies were performed, to compare the changes occurring in the analysis of longitudinal and transverse spectra.

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. In this regard, we would like to mention a thorough study on the effect of orientation on the gas permeability of LLDPE, carried out by Holden *et al.*[8], which showed a large reduction of the diffusion coefficient with increasing draw ratio. In the same way, the effect of the presence of the octene copolymer on the polyethylene properties is shown in the study carried out by Clas *et al.*[9].

## EXPERIMENTAL

The LLDPE films used in the present work were those reported by Compañ *et al.*[7]. The two films, labelled LLDPE1 and LLDPE2, were obtained by coextrusion using the same raw materials, but different processing conditions. Measurements of the thickness of the samples were performed with an LVDT Instron 8200 transducer with an accuracy of $10^{-2}\,\mu$m. The mean sample thickness was taken as the average of 20 determinations over the area of the film. The samples were subject to longitudinal and transverse induced stretching, which was always carried out at 25°C, in the ratio 2 : 1, by using an apparatus which allowed different elongational extensions to be performed.

The dynamic thermomechanical measurements to study the behaviour of the storage relaxation modulus $E'$, and loss $\tan\delta$ of the two films, were done with a PL-DMTA Mark-II apparatus using the double-cantilever inflexion method. The experiments were carried out at five differents frequencies (0.1, 0.3, 1, 3 and 10 Hz) over temperatures ranging from −140 to 100°C at a heating rate of about 1°C min$^{-1}$. During the measurements the viscoelastometer applies a sinusoidal tensile strain at one edge of the sample whose sinusoidal tensile stress response is measured at the other side of the sample. The samples were placed in the viscoelastometer longitudinally or transversely depending on the study. The value of the complex dynamic tensile modulus can be calculated from the dynamic force, while the tangent of the phase angle $\delta$ between the stress and the strain is read directly from the instrument. Changes of the real $E'$ and imaginary $E''$ parts of the complex dynamic tensile modulus $E$ and $\tan\delta$ with temperature are shown in *Figures 1–6* for each sample and direction.

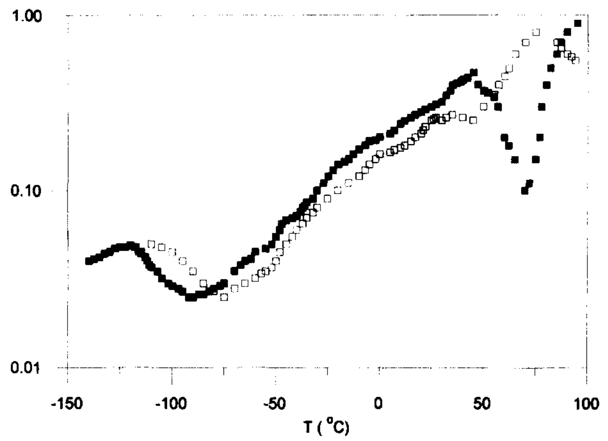

**Figure 1** Variation in the value of loss $\tan\delta$ with temperature for strips of stuck LLDPE1 (□) and LLDPE2 (■) films subject to longitudinal stretching, measured at 3 Hz

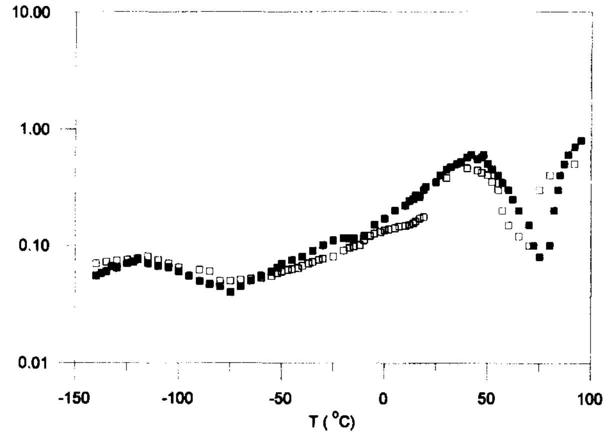

**Figure 2** Variation in the value of loss $\tan\delta$ with temperature for strips of stuck LLDPE1 (□) and LLDPE2 (■) films subject to transverse stretching, measured at 3 Hz

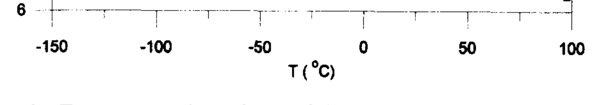

**Figure 3** Temperature dependence of the storage relaxation modulus (in pascals) for strips of stuck LLDPE1 (□) and LLDPE2 (■) films subject to longitudinal induced stretching

Experiments based on the pressure variable method were performed by using an experimental set-up that has been described elsewhere[7]. The diffusion cell we used was made taking as a model that proposed by O'Brien *et al.*[10], although in the present work only transport of pure gases is considered. Values of the gas transport coefficients of the two gases in both mentioned samples were determined in the temperature range from 25 to 85°C by the conventional time lag method. Measurements of the rate of increase in the pressure of the gas at the downstream pressure chamber, $p_{\mathrm{down}}$, and the value of the upstream pressure, $p_{\mathrm{up}}$, were obtained by means of Leybold-CM3 pressure transducers with full-scale ranges of 10 torr and $10^3$ torr, respectively. Temperature was measured and controlled with PT100 sensors with an accuracy of ± 0.1°C. The thermostat employed was a Techne TU-16D. The

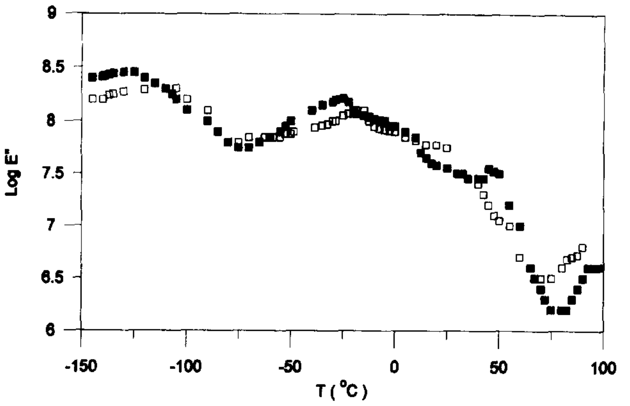

**Figure 4** Temperature dependence of the storage relaxation modulus (in pascals) for strips of stuck LLDPE1 (□) and LLDPE2 (■) films subject to transverse induced stretching

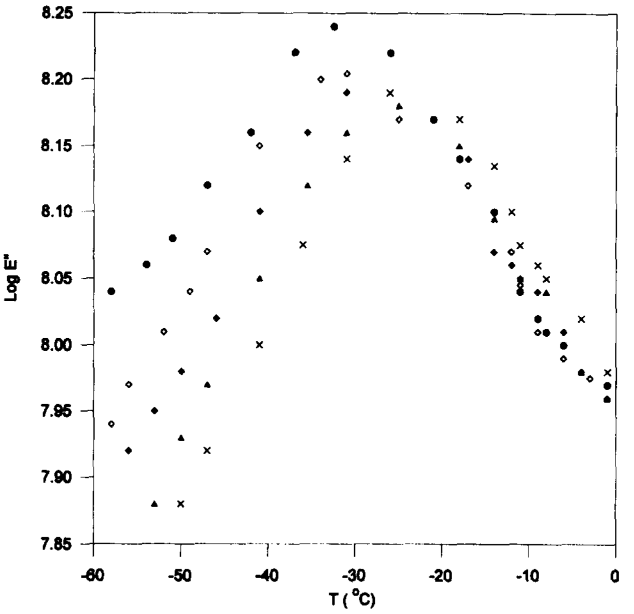

**Figure 5** Temperature dependence of the loss relaxation modulus (in pascals) for longitudinally stretched LLDPE1 film in the $\beta$ region, measured at different frequencies: 0.1 (●), 0.3 (◇), 1 (◆), 3 (▲) and 10 Hz (×)

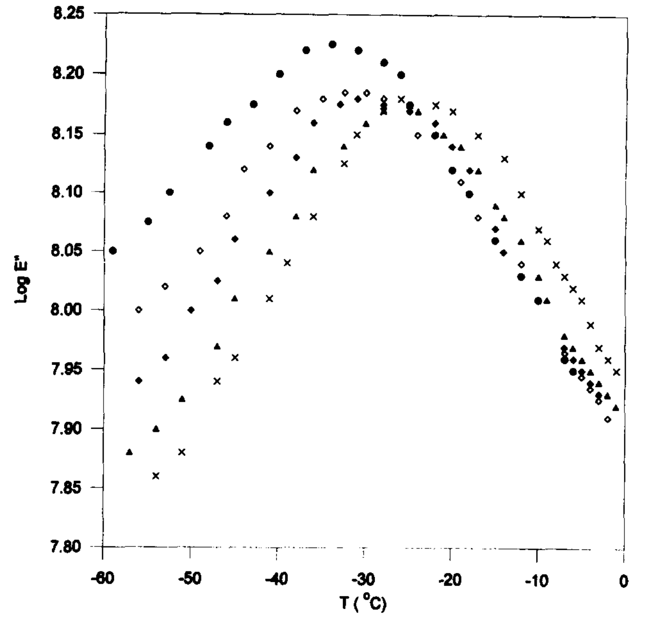

**Figure 6** Temperature dependence of the loss relaxation modulus (in pascals) for transversely stretched LLDPE2 film in the $\beta$ region, measured at different frequencies: 0.1 (●), 0.3 (◇), 1 (◆), 3 (▲) and 10 Hz (×)

area of the membrane was assumed to be the same as that of the O-ring opening which is in direct contact with the sample ($A = 5\,\mathrm{cm}^2$). The volume in the downstream reservoir was measured by using the helium expansion technique. The value of this volume was fixed at $9.0\,\mathrm{cm}^3$ by convenience in order to get downstream pressures sufficiently low in comparison with the pressure in the upstream side.

The mean permeability coefficient $\bar{P}$ was calculated from the following relationship:

$$\bar{P} = \left(\frac{L}{Ap_{\mathrm{up}}}\right)\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

where $L$ is the mean membrane thickness, $A$ is the area, $p_{\mathrm{up}}$ is the pressure at the upstream pressure side of the membrane and $\mathrm{d}Q/\mathrm{d}t$ is the rate of increase in the pressure of the permeated gas at steady state. The mean diffusion coefficient $\bar{D}$ was obtained from the time lag, $\theta$, using the relationship

$$\bar{D} = \frac{L^2}{6\Theta} \tag{2}$$

Once $\bar{P}$ and $\bar{D}$ are known, the solubility coefficient $S$ can be calculated from the following expression:

$$S = \frac{\bar{P}}{\bar{D}} \tag{3}$$

Preliminary tests of the behaviour of $\bar{P}$ and $\bar{D}$ as functions of upstream pressures were necessary in order to choose an adequate value of $p_{\mathrm{up}}$ to compare it with dynamic mechanical results and to fulfil Henry's law. A general study of the effect of pressure on gas permeation through polyethylene membranes was performed by Stern *et al.*[11]. In that work, permeability coefficients of several gases and vapours were measured at high penetrant pressures, much higher than atmospheric level. In some systems, the permeability coefficients $\bar{P}$ increased with increasing upstream pressure, and in other systems the observed behaviour was the opposite. An extension of Fujita's 'free-volume' theory of diffusion in polymers was proposed to explain the dependence of $\bar{P}$ on pressure. Similarly, Michaels *et al.*[12] measured the permeability and diffusion coefficients of gases and vapours in polyethylene membranes at atmospheric and subatmospheric pressures, between 5 and 800 torr, and no pressure dependence of the transport coefficients was observed. In the LLDPE membrane prepared from copolymers of ethylene-1-octene, in the pressure range from $10^2$ to $10^3$ torr, values of time lag from unsteady state and values of permeability from steady state in the curves of $p_{\mathrm{down}}$ *versus* time were found to be independent of $p_{\mathrm{up}}$[13]. Based on these results a value of $p_{\mathrm{up}} = 150$ torr was used in all the experiments.

Previous work on polythylene-based membranes[12,14] point out the convenience of a careful control of the thermal history of the films in order to obtain reproducible results. With this aim, the sample and the chambers in the diffusion cell were first degassed at very low pressures over 72 h to eliminate leaks and to reduce outgassing of the walls. Later, the sample was exposed to the gas at the working pressure and at a temperature of 85°C. This value was chosen because it is slightly lower than the melting point of the sample[14] and, by contrast, it is also high enough to cause considerable deviations in $\bar{P}$ values, before and after being exposed to that temperature. This thermal treatment is discussed in the next section.

## RESULTS AND DISCUSSION

The loss relaxation modulus *versus* the temperature for longitudinally stretched LLDPE films is shown in *Figure 1*. A close inspection of the plots in the $\alpha$ region reveals that the positions of the $\alpha'$ and $\alpha''$ peaks are almost the same as that found in a previous study[7]. The $\alpha'$ relaxation process is centred at 30°C, whereas the $\alpha''$ relaxation process is centred at 50 and 80°C for LLDPE1 and LLDPE2, respectively. The spectra, expressed in terms of the loss $\tan\delta$, for transversely stretched LLDPE films can be seen in *Figure 2*. The intensity of the peak associated with the $\alpha'$ relaxation is lowered for both polyethylenes. The peak related to the $\alpha''$ relaxation is located in the interval 40–50°C for both LLDPE films. The $\alpha$ relaxation process is produced by motions of the chain folds at the crystal surface. It should be pointed out in connection with this that although the $\alpha$ process occurs in the amorphous phase, its development may require some mobility of the crystals. Studies carried out by Mandelkern and co-workers[15] have treated the $T_\alpha$ dependence on the thickness of the crystallites, showing that $T_\alpha$ increases as the thickness increases. On the other hand, these studies suggest that more than a single $\alpha$ peak can be developed by controlling the crystallite thickness and distribution. According to this, the $\alpha'$ and $\alpha''$ peaks may result from two groups of crystallites of slightly different developed thickness in the A and B layers[7].

The activation energies associated with the $\alpha'$ peak in the relaxation spectrum of stretched LLDPE could not be obtained accurately from the experimental results except in the case of longitudinally stretched LLDPE1, in which case it amounts to $46.8 \pm 0.5\,\mathrm{kcal\,mol^{-1}}$. The activation energies for the $\alpha''$ process in the longitudinally stretched membranes are $95 \pm 1$ and $103 \pm 2\,\mathrm{kcal\,mol^{-1}}$ in LLDPE1 and LLDPE2, respectively. The corresponding values for the transversely stretched membranes are $90 \pm 2$ and $105 \pm 3\,\mathrm{kcal\,mol^{-1}}$ in LLDPE1 and LLDPE2, respectively.

*Figures 3* and *4* show the variation of $\log E''$ *versus* $T$ for LLDPE1 and LLDPE2 subject to longitudinal and transverse stretching. It may be noted that the curves are quite similar for both films, unlike the values of the modulus for LLDPE1 and LLDPE2, which are slightly different, depending on whether the films are subject to longitudinal or transverse stretching.

Information about the $\gamma$ and $\beta$ regions was obtained from thermomechanical analysis. It is well known that in the $\beta$ region the relaxation process is produced by movements around the amorphous zone. These movements are, usually, micro-Brownian, being a consequence of the relaxation process between the glass and rubber phases[16–18]. The values of the activation energy corresponding to the second peak of the $\beta$ relaxation of LLDPE1 and LLDPE2 subject to longitudinal stretching are $61.5 \pm 0.5$ and $60.9 \pm 0.5\,\mathrm{kcal\,mol^{-1}}$, respectively. On the other hand, in LLDPE1 and LLDPE2 subject to transverse stretching, the results obtained are $65.2 \pm 0.5$ and $63.4 \pm 0.5\,\mathrm{kcal\,mol^{-1}}$, respectively. These values have been obtained from *Figures 5* and *6*.

No significant changes have been found in the location and the shape of the $\gamma$ relaxation with respect to the conventional LLDPE[19]. However, we want to point out that a slight displacement of 5°C in the LLDPE1 with respect to the LLDPE2 takes place when the films are subject to longitudinal stretching. The opposite is found in the transversely stretched film, where $\tan\delta$ is slightly greater for LLDPE1 than for LLDPE2. The same behaviour is observed in the plot $\log E''$ *versus* $T$. The activation energy of the $\gamma$ relaxation is $18.0 \pm 0.5$ and $20.0 \pm 0.5\,\mathrm{kcal\,mol^{-1}}$ for the longitudinally stretched LLDPE1 and LLDPE2 films, respectively. In the transversely stretched LLDPE1 and LLDPE2 films, the corresponding values are $20.0 \pm 0.5$ and $22.0 \pm 0.5\,\mathrm{kcal\,mol^{-1}}$, respectively.

The experiments of diffusion and permeability have been carried out in the region of the $\alpha$ relaxation process, that is to say, from 25 to 85°C, employing the pressure variable method. The major difficulty is the strong dependence of polymeric properties on the prior history of the film. The influence of the previous thermal history on transport coefficients was observed in all polyethylene membranes and for the two gases studied. The treatment at a high temperature is always necessary in order to obtain reproducible results. This treatment involved heating the film to 85°C for about 2 h, subsequently cooling it in an air chamber immersed in a water bath. As can be seen by comparing *Figures 7a* and *7b*, this thermal treatment erased the previous history. In *Figure 7a* is shown the permeability of $O_2$ as a function of the temperature, when the film was not subject to a previous thermal treatment. Experiments start and finish in the limit of low temperature. As can be seen, significant differences in $\bar{P}$ values are found. This difference is greater when the temperature is decreased. On the other hand, in *Figure 7b*, permeability values of $O_2$ in a film with previous thermal treatment do not show any significant difference. The same behaviour has been observed independently of the gas employed as the permeant. A more rigorous study of this effect will be reported in a subsequent paper.

*Figures 8* and *9* show the dependence on the temperature of mean permeability and diffusion coefficients, respectively, in LLDPE1 and LLDPE2 membranes. The shape and evolution of the permeability and diffusion curves are nearly the same for both gases and in both polyethylenes. Likewise, the $\bar{P}$ and $\bar{D}$ values for $CO_2$ are larger than those corresponding to $O_2$ in both LLDPE1 and LLDPE2, while the values in LLDPE1 are lower than those in LLDPE2. Breaks in the Arrhenius plots of $\bar{P}$ and $\bar{D}$, in both samples and with both gases, can be observed. The break temperature, $T_b$, is found to be in the range from 51 to 55°C, in all cases. This effect is less evident in the diffusion than in the permeability curves and less significant in $O_2$ than in $CO_2$. Also, this effect is smaller in sample 1 than in sample 2. On the other hand, the same relative behaviour of the two gases is found at the temperature of glass transition in poly(ethylene teraphthalate)[20], showing that this result is independent of the presence of octene in the copolymer.

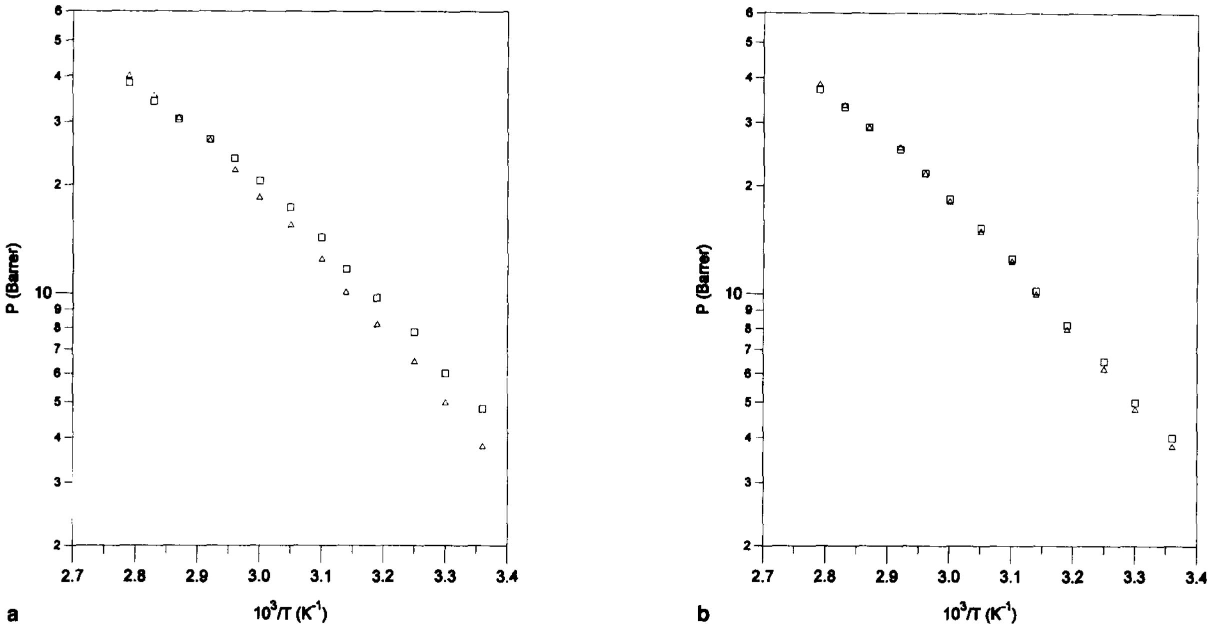

**Figure 7** (a) Permeability coefficient of $O_2$ in an LLDPE film without previous thermal treatment. (b) Permeability coefficient of $O_2$ in an LLDPE film with previous thermal treatment

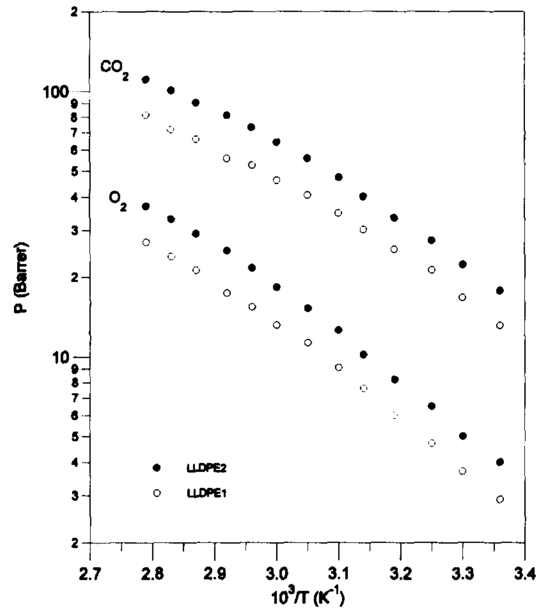

**Figure 8** Permeability coefficient of $CO_2$ and $O_2$ in LLDPE membranes *versus* the reciprocal absolute temperature

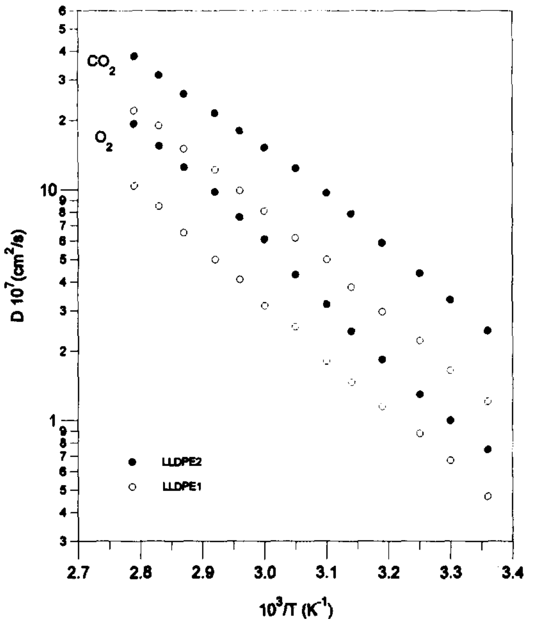

**Figure 9** Diffusion coefficient of $CO_2$ and $O_2$ in LLDPE membranes *versus* the reciprocal absolute temperature

In the same way, it is observed that below $T_b$ the values of the diffusion coefficient obtained by the pressure variable method are almost the same as those reported for LLDPE in the absence of octene[21]. However, mean permeability values in the cases studied here were higher than in membranes without the comonomer; this can be reasonably associated to a change in the gas solubility due to the presence of the octene in the membrane.

The curves depicting the temperature dependence of the permeability coefficient of both $O_2$ and $CO_2$ through the LLDPE1 and LLDPE2 longitudinally and transversely stretched films are shown in *Figures 10* and *11*, respectively. In the case of longitudinally stretched films, the permeation response is the same for the two samples. Likewise, the $\bar{P}$ values for $CO_2$ are significantly larger than those corresponding to $O_2$ throughout the temperature range. In the transversely stretched films no differences are observed between LLDPE1 and LLDPE2, below $T_b$. However, above $T_b$, $\bar{P}$ values measured are larger in LLDPE1 than in LLDPE2. The greater differences found are, approximately, 15% for $O_2$ and 10% for $CO_2$. As in the longitudinally stretched films, $\bar{P}$ values for $CO_2$ are appreciably larger than $O_2$ values. On the other hand, breaks in the Arrhenius plots can also be observed, although the change in slope is less remarkable than in the corresponding unstretched films. Values of $T_b$ are significantly lower when the membranes are transversely stretched than when they are longitudinally stretched. The temperature range of $T_b$ is from 43 to 51°C for both gases and in both types of films.

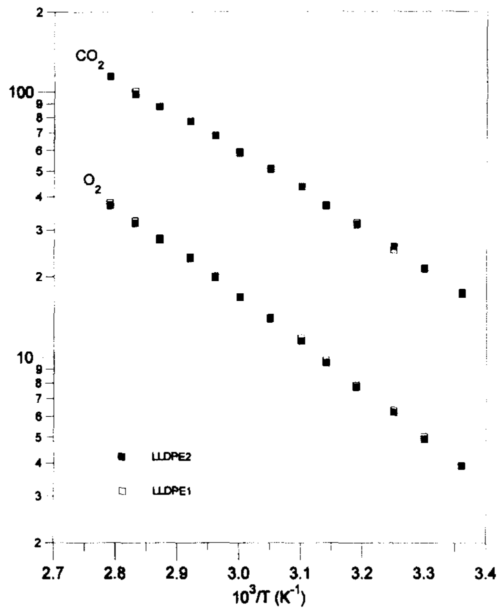

**Figure 10** Permeability coefficient of $CO_2$ and $O_2$ in longitudinally stretched LLDPE membranes

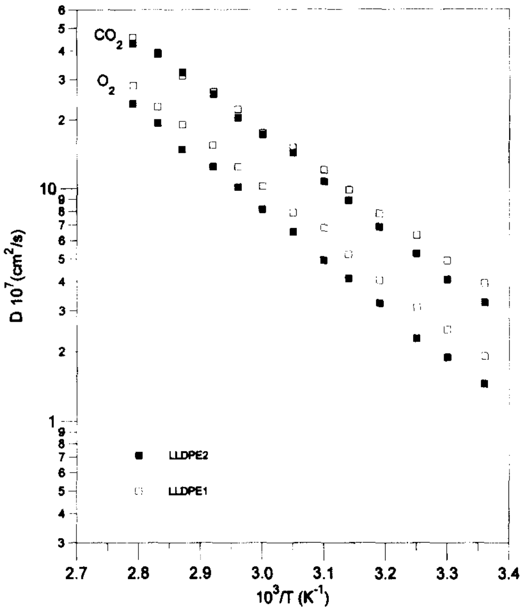

**Figure 12** Diffusion coefficient of $CO_2$ and $O_2$ in longitudinally stretched LLDPE membranes

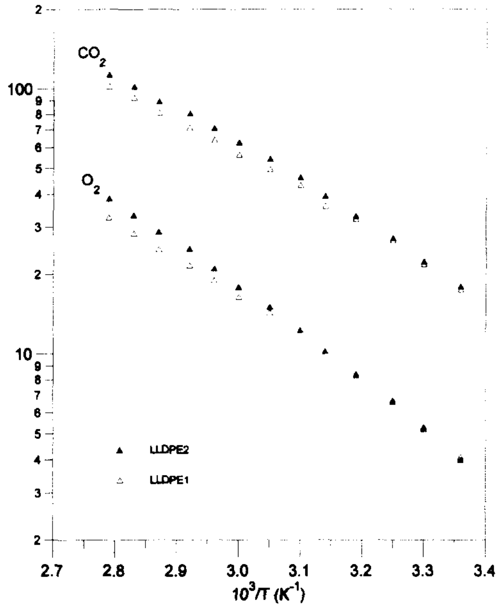

**Figure 11** Permeability coefficient of $CO_2$ and $O_2$ in transversely stretched LLDPE membranes

In *Figures 12* and *13*, we show the diffusion dependence on the temperature, expressed by Arrhenius plots, of both $O_2$ and $CO_2$ in LLDPE1 and LLDPE2 films subject to both kinds of stretching. The diffusion coefficients of $O_2$ are lower than those corresponding to $CO_2$ in all systems studied and in all the temperature range. Similarly, the diffusion coefficients of $O_2$ in longitudinally and transversely stretched LLDPE1 film are higher than in stretched LLDPE2 at every temperature. In some cases, this difference reaches levels of up to 25%. In the case of $CO_2$, the same behaviour is observed; however, the difference between the diffusion values in stretched LLDPE1 and stretched LLDPE2 is smaller. This is probably due to a plastificant effect of $CO_2$ in the films[22,23]. On the other hand, breaks can also be observed. These breaks are more significant in the polyethylene films subject to transverse stretching than in the longitudinally stretched film. This behaviour is independent of the gas employed as the permeant, $O_2$ or $CO_2$. It seems that when the stretching is in the same direction as the drawing, the change in the slope of the Arrhenius plots is less evident.

The effect of stretching in modifying the permeation response of LLDPE1 and LLDPE2 as a function of the temperature is shown in *Figures 14* and *15* (obtained from the comparison of *Figures 10* and *11* with *Figure 8*). These figures refer to $O_2$/LLDPE1 and $CO_2$/LLDPE2 systems subject to both kinds of stretching. Although only these systems are used for illustration, the rest of the systems exhibited the same behaviour. A significant increase throughout the temperature range can be observed in the case of the LLDPE1 membrane when it is subject to stretching. This increase is almost the same for the two gases: 25–35%. The change observed in the LLDPE2 membrane for the two gases is less noticeable; this change was never greater than 10%. In all cases studied, the permeability coefficients in stretched membranes are almost the same, independent of the direction of stretching.

Comparing *Figures 12* and *13* with *Figure 9* (*Figures 16* and *17*), the effect of stretching on the diffusion coefficient in the two systems mentioned above can be observed. The effect of stretching on the diffusion in the rest of the systems is nearly the same as that shown in these figures. In the case of the LLDPE1 membrane, the stretching, independently of the direction, produces an important increase in the diffusion coefficient of both $O_2$ and $CO_2$. A less significant increase is observed in the stretched LLDPE2 membrane. This is the same behaviour that is observed in permeation response.

These changes of permeability and diffusion may reflect the change of the extruded-induced order by the stretching. Presumably, the stretching produces a molecular reorientation in the crystalline–amorphous interfaces. It seems that the diffusion coefficient is more sensitive to morphological changes than the permeability coefficient.

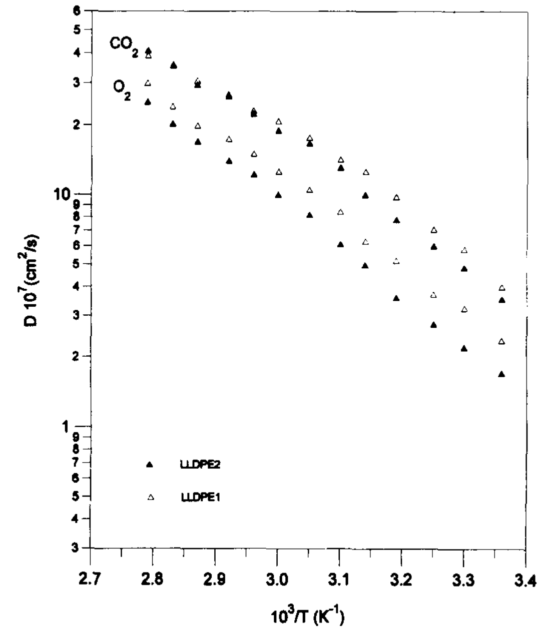

**Figure 13** Diffusion coefficient of $CO_2$ and $O_2$ in transversely stretched LLDPE membranes

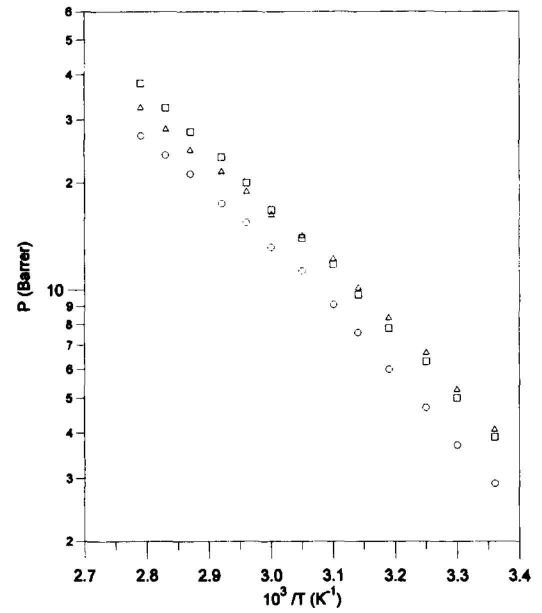

**Figure 14** Effect of both kinds of stretching in the permeability of $O_2$ through LLDPE1 in unstretched film (O), longitudinally stretched film (□) and transversely stretched film (△)

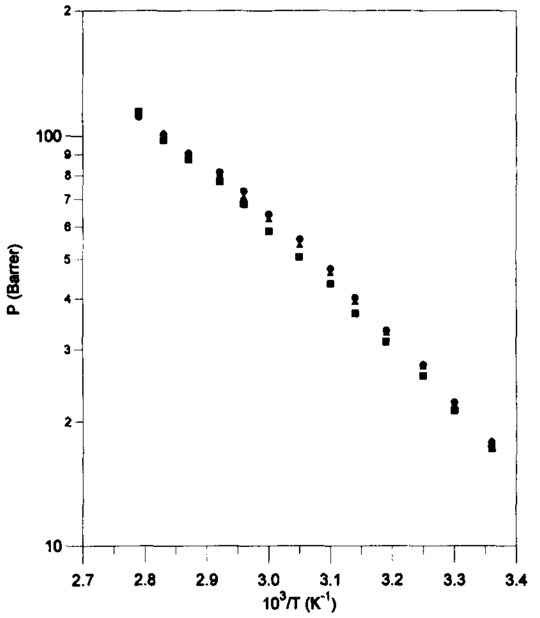

**Figure 15** Effect of both kinds of stretching in the permeability of $CO_2$ through LLDPE2 in unstretched film (●), longitudinally stretched film (■) and transversely stretched film (▲)

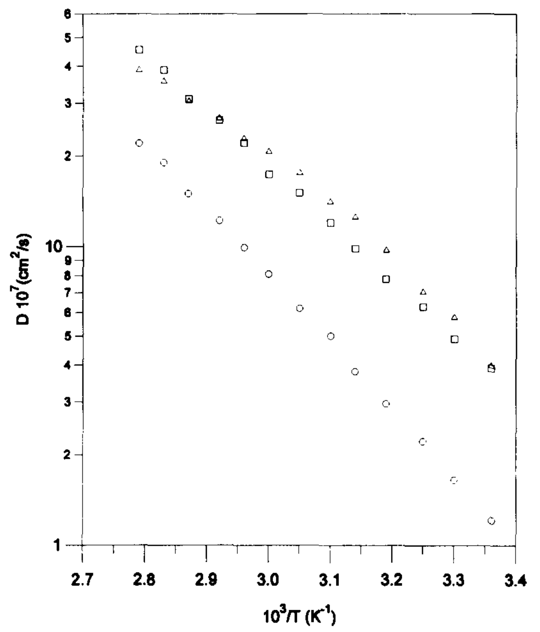

**Figure 16** Diffusion of $O_2$ in unstretched LLDPE1 film (O), longitudinally stretched LLDPE1 film (□) and transversely stretched LLDPE1 film (△)

The activation energies associated with the permeation and diffusion of $O_2$ and $CO_2$ in unstretched LLDPE membranes are presented in *Table 1*. To obtain these values it is conventionally assumed that a thermally activated process follows the Arrhenius equation:

$$X = X_0 \exp\left(\frac{-E_X}{RT}\right) \tag{4}$$

where $X$ can be either the permeability or diffusion coefficients, $\bar{P}$ or $\bar{D}$, $X_0$ is a constant ($P_0$ or $D_0$), which is characteristic of the polymer–gas system, and $E_X$ is the activation energy ($E_P$ for permeability and $E_D$ for diffusion). Values of $E_x$ are collected in the tables, calculated from the slope of the straight line $\ln X$ *versus* $T^{-1}$ plot, below and above $T_b$.

As may be seen in *Table 1*, both activation energies, $E_P$ and $E_D$, show a decrease above $T_b$ in all cases studied. The error in the determination of $E_D$ is bigger than in $E_P$, reflecting the difficulty in measuring accurately the small values of the time lag. The values of $E_P$ for $CO_2$ are lower than those corresponding to $O_2$, above and below $T_b$, in the two samples studied. No differences are found, however, between the values obtained for LLDPE1 and those corresponding to LLDPE2 for each gas. In the case of diffusion, the values of $E_D$ show some differences between the two films. The $E_D$ values obtained are

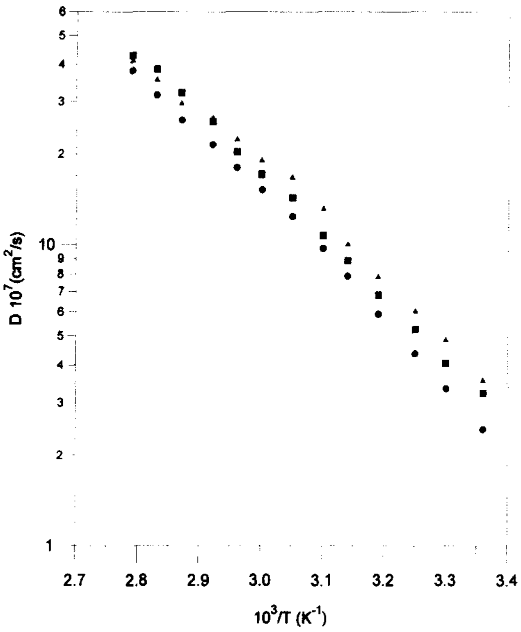

**Figure 17** Diffusion of $CO_2$ in unstretched LLDPE2 film (●), longitudinally stretched LLDPE2 film (■) and transversely stretched LLDPE2 film (▲)

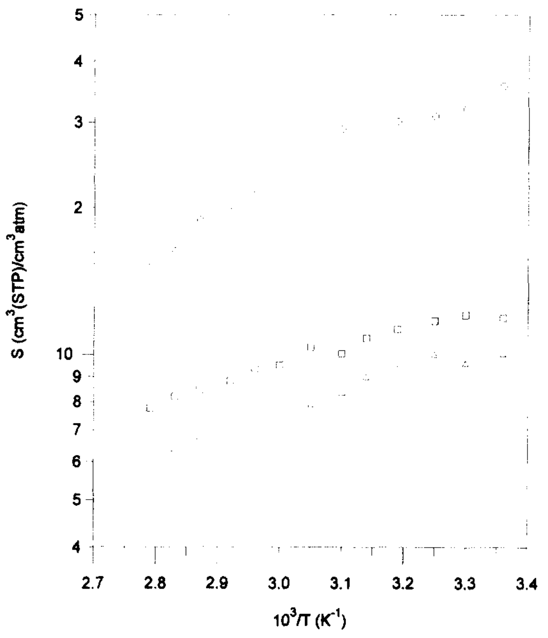

**Figure 18** Effect of both kinds of stretching in the solubility of $O_2$ in LLDPE1 in unstretched film (○), longitudinally stretched film (□) and transversely stretched film (△)

**Table 1** Activation energies for permeation $E_P$ and diffusion $E_D$ and heats of solution $\Delta H_S$ of $O_2$ and $CO_2$ in unstretched LLDPE films

| | | $E$ (kcal mol$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Permeability | | Diffusion | | Solubility | |
| Film | Temperature interval (°C) | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ |
| LLDPE 1 | 25–55 | 8.8 | 7.3 | 9.7 | 10.3 | −1.5 | −2.4 |
| LLDPE 2 | 25–55 | 8.7 | 7.4 | 10.1 | 10.5 | −1.6 | −2.8 |
| LLDPE 1 | 60–85 | 6.8 | 5.2 | 8.2 | 8.5 | −1.6 | −1.8 |
| LLDPE 2 | 60–85 | 6.5 | 5.2 | 9.3 | 8.5 | −2.8 | −3.0 |

**Table 2** Activation energies for permeation $E_P$ and diffusion $E_D$ and heats of solution $\Delta H_S$ of $O_2$ and $CO_2$ in longitudinally stretched LLDPE films

| | | $E$ (kcal mol$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Permeability | | Diffusion | | Solubility | |
| Film | Temperature interval (°C) | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ |
| LLDPE 1 | 25–55 | 8.2 | 6.7 | 10.0 | 8.6 | −1.2 | −1.9 |
| LLDPE 2 | 25–55 | 8.2 | 7.0 | 9.6 | 9.2 | −1.2 | −2.6 |
| LLDPE 1 | 60–85 | 7.6 | 6.2 | 9.1 | 8.4 | −1.9 | −1.7 |
| LLDPE 2 | 60–85 | 7.5 | 5.6 | 9.8 | 8.8 | −2.6 | −3.3 |

**Table 3** Activation energies for permeation $E_P$ and diffusion $E_D$ and heats of solution $\Delta H_S$ of $O_2$ and $CO_2$ in transversely stretched LLDPE films

| | | $E$ (kcal mol$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Permeability | | Diffusion | | Solubility | |
| Film | Temperature interval (°C) | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ |
| LLDPE 1 | 25–55 | 8.3 | 6.7 | 9.4 | 9.7 | −1.7 | −3.4 |
| LLDPE 2 | 25–55 | 8.5 | 7.1 | 10.1 | 9.8 | −2.5 | −3.1 |
| LLDPE 1 | 60–85 | 6.3 | 5.6 | 7.9 | 6.5 | −3.6 | −3.2 |
| LLDPE 2 | 60–85 | 7.2 | 5.6 | 8.3 | 6.9 | −3.5 | −3.1 |

slightly lower in LLDPE1 than in LLDPE2 for $O_2$. A comparison of these results with that corresponding to LLDPE without octene[21] show that while $E_D$ values below $T_b$ are practically the same, the $E_P$ are significantly lower in our experiment, basically in the $CO_2$ case.

$E_P$ and $E_D$ values in longitudinally and transversely stretched films obtained from Arrhenius plots are shown in *Tables 2* and *3*. It can be seen, as in unstretched films, that $E_P$ values for $O_2$ are larger than $E_P$ values for $CO_2$ throughout the temperature range. In the case of LLDPE2 films, $E_P$ values obtained for each gas are almost the same regardless of the direction of the stretching. A similar behaviour is observed for LLDPE1 films below $T_b$. Above $T_b$, however, $E_P$ is slightly lower in the transversely stretched film than in the longitudinally stretched one. On the other hand, $E_D$ values for $O_2$ are larger than those calculated for $CO_2$, just as with the permeability energies. It can be observed that the stretching does not show a definite trend in the diffusion energies.

On the other hand, it is of interest to study the effect of stretching on the gas solubility in the polyethylene membranes. As in the preceding cases, the solubility coefficients in the $O_2$/LLDPE1 and $CO_2$/LLDPE2 systems are presented in *Figures 18* and *19*. The systems shown in these figures are illustrative of the general observed behaviour.

It can be seen that the $CO_2$ solubilities in both unstretched polyethylene membranes are higher than those obtained for $O_2$ in all the temperature range studied. This is the same behaviour observed by Michaels and Bixler[12] in Alathon 14 polyethylene membranes.

The effect of temperature on solubility coefficients over the range studied is given by the usual Arrhenius expression (equation (4));

$$S = S_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \qquad (5)$$

where $X$ is the solubility coefficient $S, X_0$ is a constant ($S_0$) and $E_X$ is the heat of solution ($\Delta H_S$). The $\Delta H_S$

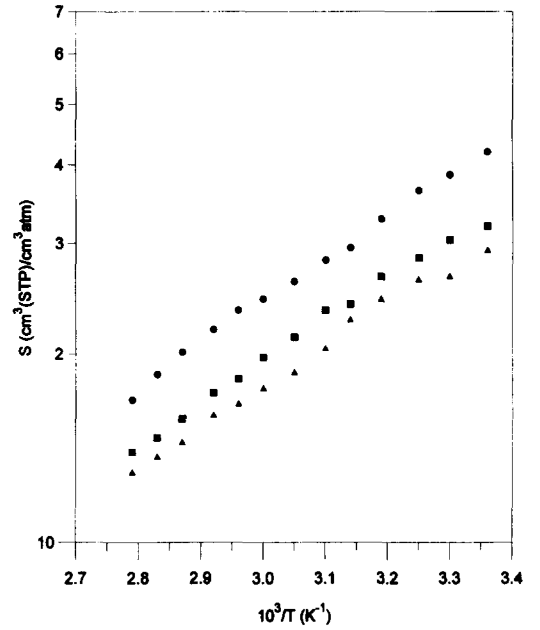

**Figure 19** Effect of both kinds of stretching in the solubility of $CO_2$ in LLDPE2 in unstretched film (●), longitudinally stretched film (■) and transversely stretched film (▲)

values obtained this way are presented in *Table 1*. It can be seen that the heats of solution are exothermic in all systems studied. This is the opposite behaviour to that observed by Michaels and Bixler for $O_2$ and $CO_2$ in Alathon 14 polyethylene membranes; in that case the heat of solution was positive. However, studies carried out by Barrie *et al.*[20] have shown that the addition of comonomers to polyethylene polymers made $\Delta H_S$ negative.

The solubility in the stretched membranes is presented in *Figures 18* and *19*. The $CO_2$ solubilities are still higher then those for $O_2$. As in the case of permeability and diffusion coefficients, the effect of stretching, irrespective of the direction of its application, is more noticeable in the LLDPE1 membrane. And in all systems studied, the stretching produces a reduction in the solubility coefficients. The temperature dependence of the solubility coefficients in stretched membranes was found to obey the same relationship as in the unstretched membranes. The heats of solution are presented in *Tables 2* and *3*. It can be seen that these values are exothermic, but they are lower than those exhibited in unstretched membranes.

It should be pointed out, comparing the results obtained in the dynamic thermomechanical and diffusive studies, that the breaks observed in the Arrhenius plots of permeability and diffusion in the stretched polyethylene membranes (*Figures 10–13*) in the interval 43–51°C could be related to the $\alpha''$ peaks found in the curves of loss $\tan\delta$ *versus* $T$. The $T_{\alpha''}$ temperatures obtained from relaxation spectra are compared to $T_b$ temperatures from permeability measurements. The only disagreement observed in the results of both methods is the high temperature at which the $\alpha''$ relaxation appears in the longitudinally stretched LLDPE1 film. These facts lead to the conclusion that the breaks observed in the permeability and diffusion curves may be caused by an $\alpha$ relaxation process. On the other hand, $\alpha'$ peaks which appear in the results obtained from dynamic mechanical measurements are not clearly observed in the permeability results. The separation of the $\alpha$ relaxation process into two peaks $\alpha'$ and $\alpha''$ results from the existence of two groups of crystallites of different thickness and distribution that developed in the A and B layers. These differences are so small that permeability measurements do not seem to be a useful tool to detect the $\alpha'$ relaxation. Similarly, in the results from the dynamic mechanical study it can be observed that the $\alpha'$ absorption is much lower than the $\alpha''$ absorption in stretched polyethylene films.

## CONCLUSIONS

Dynamic mechanical results reveal that stretching does not produce any significant changes in the location of the temperatures at which the LLDPE presents its $\gamma$ and $\beta$ relaxation processes, whereas in the $\alpha$ region a significant displacement of the location of the $\alpha''$ relaxation is observed when the film is subject to longitudinal stretching. Likewise, transverse stretching gives rise to a decrease in the intensity of the peak associated with the $\alpha'$ relaxation.

The transport coefficients obtained from the pressure variable method are influenced by the previous thermal history of the membrane. A high-temperature treatment is always necessary in order to obtain reproducible results.

On the other hand, the presence of octene increases the permeability of $O_2$ and $CO_2$ in polyethylene films and, therefore, a reduction in the activation energy of permeation is observed. As the diffusivity and the energy related to the diffusion process are almost the same as that found in conventional polyethylene, this behaviour is associated with a change in the gas solubility.

The Arrhenius plots of $\bar{P}$ and $\bar{D}$ show a break in the range from 51 to 55°C in the two types of unstretched polyethylenes and for the two gases. The stretched membranes show this break in the temperature range 43–51°C. This break is probably caused by an $\alpha$ relaxation process.

Both forms of stretching cause an increase in the diffusion coefficients and a reduction in the solubility coefficients, and the overall effect is an increase in the permeability coefficients. This behaviour is presumably due to a change of the molecular orientation in the crystalline–amorphous interfaces. This change has been observed for both gases, and it is more important in the LLDPE1 sample.

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