Permeation of carbon dioxide through multiple linear low-density polyethylene films

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Abstract

We have investigated the effect of stacking on the permeation of carbon dioxide through multilayer LLDPE films. The measurements were carried out using samples made up of one, two, four, eight and 12 films, respectively, over the temperature interval of 25–85°C. The results indicate that the permeability coefficient $P$ of carbon dioxide does not show any variation on the number of films stacked. In contrast, the time lag values increase in a non-linear way with increasing the number of films in the samples. The analysis of these results, according to gas permeation models through multilayer systems, shows that boundary effects at the interface between films are not found, on the one hand, and the experimental values determined for the time lags are in good agreement with the theoretical predictions, on the other hand. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Permeability is not a property of the membrane, it is a phenomenological coefficient. Although it is well known that the value of permeability is a function of temperature and pressure, it is less understood that permeability can also vary with the thickness of the membrane. When the observed permeability changes as a function of membrane thickness, there are two possible reasons [1–3]. One is the presence of boundary layers or interfacial resistances. The other is the variation of permeability throughout the membrane, as in the case of laminated composite membranes. When the membrane exhibits a structure consisting of two or more different layers, the observed overall permeability becomes a function of membrane thickness. Moreover, the relationship between permeability and diffusivity also becomes complicated and involves the membrane thickness.

Frisch considered the steady-state flux of a gas and permeability through a membrane composed of two or more parallel films [4]. He developed a relatively simple procedure that permits to obtain a relationship between the observed overall permeability and the permeability coefficients of the individual films composing the membrane. It showed that the permeability coefficient of a composite membrane is given by the harmonic average of properly weighted permeability coefficients of the individual layers, the weight being the ratio of the thickness of the individual layer to the total thickness of the sample.

In the case of problems involving composite membranes, the full solution of the diffusion equation in each layer and in the transient state is too involved for convenient application in the derivation of time lags.
However, methods have been developed which enable time lags to be determined without obtaining complete solutions of the diffusion equations [5,6]. General formulae have been obtained for any number of layers in the form of slabs, hollow cylinders or spherical shells [7].

In recent publications [8–12], the permeability properties exhibited by coextruded linear low-density polyethylene (LLDPE) membranes were measured using both an electrochemical technique and the time-lag permeation method. It was found that, under experimental conditions, there is no appreciable dependence of the permeability and diffusion coefficients on pressure. Studies of the temperature dependence of both the permeability and diffusion coefficients showed a strong sensitivity of these coefficients to the melting and recrystallization processes, which occur in these membranes at high temperatures. These processes alter the morphology of the film and, as a result, its diffusional characteristics. The influence of the orientation of the membranes on the gas transport properties through them was examined by mean of permeation measurements. The experiments were carried out with oriented membranes elongated by a factor of two, either in the longitudinal or transverse directions to the processing orientation of the membranes. It showed that orientation produced a slight decrease of the permeability through membranes. This reduction was associated to a microstructural transformation that took place when the membranes are oriented. Nevertheless, the results indicated that the main transport mechanism in both, longitudinally and transversely oriented membranes, is of the same type as that found in unoriented membranes, i.e., of the solution-diffusion type.

Owing to the widespread use of LLDPE membranes in the packaging industry, it is necessary to investigate the gas transport properties of strips made up of membranes that have been firmly stuck together. Therefore, in the present work we study the thickness effect on both permeability coefficients and time lag values, and the results are compared with the theoretical predictions from earlier studies.

2. Experimental

2.1. Characteristics of the LLDPE films

The films used in this work are made of 1-octene-co-ethylene copolymers with roughly 8% mol content of the first comonomer [12]. The films were coextruded with three extruders C, A, and B at speeds of 88, 29, and 88 rpm, respectively. As a consequence, the films were made up of three layer, i.e., C (15 wt%) A (70 wt%) B (15 wt%). The thickness of the films was 21 μm. The die-exit temperature was 270°C, and the distances between the die and the chill roll (cooled with water at 20°C), and between the die exit and the frost line were, respectively, 15 and 155 mm. Finally, the vacuum knife depression and the line speed were, respectively, 3.5 cmHg and 200 rpm.

The thermal behaviour of the films was determined with a Perkin–Elmer DSC-4 calorimeter at a heating rate of 8°C min⁻¹. The thermogram of the films shows a wide melting endotherm that extends from 90 up to ca 127°C with the maximum of the peak located at ca 122°C. The degree of crystallinity of the films, determined from the melting endotherms by assuming that the melting enthalpy is 960 cal (mol CH₂)⁻¹, was 0.24.

The crystallinity of the film was also determined by Raman spectroscopy using a Ramanor U 1000 double monochromator equipped with two 1800 mm⁻¹ planar holographic gratings. The spectra present two peaks centered at 1418 and 1077 cm⁻¹, which are considered to be associated with the crystalline and amorphous phases, respectively. By comparing the intensities of these peaks with that of the peak located at 1296 (independent of the morphology of the films), the results show that the crystallinity-amorphous fraction of the films is 0.24/0.60. According, the fraction interfacial material amounts to 0.16.

The films exhibit birefringence as a consequence of their orientation in the direction of extrusion. The value Δn, measured with an Amplival Pol microscope at room temperature, was 2.9 × 10⁻³.

2.2. Equipment and procedures

The experimental device used was essentially similar to those described previously in earlier works [8–12]. The central element of the experimental set-up is a diffusion cell, which basically encompasses two equal cylindrical parts made of stainless steel and designed taking as a model that proposed by O’Brien et al. [13]. Each membrane subject to study was placed inside the cell and two O-rings were employed to ensure that there were no leaks. The cell, which was connected with both the vacuum system and the gas supplier, and the major part of the assembly were placed under the water contained in a thermostat bath. The temperature requirements were set by a Techne TU-16D thermostat. Measurements of the pressure were obtained by means of two Leybold-CM3 pressure transducers with full-scale ranges of 1 cmHg and 10² cmHg.

The minimum purity for CO₂ was 99.998% and no further purification was attempted before admission to the experimental apparatus.

Transport measurements were performed in mem-
branes made up of several LLDPE films firmly stacked. The stacking of the films was made at room temperature. The films were compressed with a rolling cylinder in order to make sure that the free space between them was the less possible. In particular, samples containing one, two, four, eight and 12 films were employed. The thickness of the samples was measured with an LVDT Instron 8200 transducer. Table 1 contains the mean sample thickness for each case, which was taken as the average of 20 determinations over the surface of the membrane.

The transport properties of pure CO₂ through the samples were determined using the time lag permeation method. The measurements were carried out over the temperature interval from 25 to 85°C, while the upstream pressure was kept at about 20 cmHg in all the experiments. The permeability coefficient \( P \) was calculated from the expression:

\[
P = \frac{273}{76} \frac{V}{A} \frac{dp_{\text{down}}}{dt}
\]

where \( V \) is the volume occupied by the permeate gas, in cm\(^3\); \( T \) is the temperature of this gas, in K; \( A \) and \( l \) are the area and thickness of the sample, in cm\(^2\) and cm, respectively; \( p_{\text{up}} \) is the applied gas pressure, in cm Hg; and \( dp_{\text{down}}/dt \) is the rate of increase in the pressure of permeated gas at steady state, in cm Hg s\(^{-1}\). \( P \) is given, accordingly, in units of Barrer \( [10^{-10} \text{ cm}^3 \text{ cm Hg}^{-1} \text{ s}^{-1}] \), as used by many investigators \([14,15]\). In all permeability measurements the maximum of \( p_{\text{down}} \) was not allowed to exceed 1% of \( p_{\text{up}} \). The time lag values were determined by the extrapolation of the steady state part of the permeation curve to the time axis. The errors involved in the determination of the time lag values will be discussed later.

3. Results and discussion

Measurements of the permeability coefficients of CO₂ were carried out in samples containing one, two, four, eight and 12 films. The permeation experiments were performed in a temperature range from 25 to 85°C. The effect of thickness on the permeability coefficient is shown in Fig. 1. In this Figure, only values obtained at four temperatures are plotted for simplicity. As it is seen in Fig. 1, no thickness dependence of the permeability is discernible.

The inspection of possible boundary effects at the interface between films can be made on the basis of the electric circuit analogy \([2,16]\). The method considers that each layer in the membrane and the boundary layers presents its own resistance to the mass transport. The total resistance to the permeation consists of resistances of different laminates and those of boundary layers or interfaces. When \( \Delta p/J \) is plotted against membrane thickness, several segments of straight lines will result, where \( \Delta p = p_{\text{up}} - p_{\text{down}} \), and \( J \) is the gas flow through the sample. The permeability of a particular layer can be obtained from the slope of each straight line and the intercept gives the boundary resistances. As it can be seen in the example given in Fig. 2, plots made according to this procedure show that just one straight line. This behaviour was expected since the multilayer samples are made up of the same type of films. In addition, boundary effects at the interface between films are not detected, as indicated by the fact that the intercept with thickness axis equals zero.

Fig. 3 shows the experimental values obtained for the time lags in different multilayers of LLDPE films at different temperatures. It can be observed that if the number of the stacked films increases, that is to say, the thickness of the sample increases, the time lag increases at all temperatures of interest. Owing to the value of diffusion coefficient of carbon dioxide in LLDPE, significant errors may be involved in the measurements of \( \theta \), especially in the thinner samples and in the limit of high temperatures. Actually, the smaller the thickness, the lower the \( \theta \) and, consequently, the larger the uncertainty of the value of the resulting \( \theta \). It should be pointed out that the time lags were obtained from two consecutive measurements carried out on the samples, and the results were carefully checked. However, the relative error involved in the determination of \( \theta \) reached ca 100% in some cases. In view of these significant errors, arising from the high value of \( D \) in the films, it seemed more advisable that all these time lag values were eliminated from further consideration.

Earlier studies carried out on the diffusion of gases in multilayer membranes showed that the relation between the time lag at the whole multilayer system, \( \theta \), and that of a single layer, \( \theta_1 \), is given by [6]:

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### Table 1

Thickness of multilayer LLDPE films

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>1 film</th>
<th>2 films</th>
<th>4 films</th>
<th>8 films</th>
<th>12 films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21.0 ± 0.1</td>
<td>43.6 ± 0.4</td>
<td>87.7 ± 0.2</td>
<td>178 ± 2</td>
<td>271 ± 4</td>
</tr>
</tbody>
</table>
Fig. 1. Variation of the permeability coefficient of carbon dioxide through LLDPE samples with their thickness at different temperatures. ◇, 298 K; ▲, 313 K; ■, 328 K; ●, 343 K.

Fig. 2. Thickness analysis for carbon dioxide permeation in multilayer LLDPE films.
\[
\theta = \left[ \sum_{i=1}^{n} \left( \frac{l_i}{D_i} \prod_{j=0}^{i-1} k_j \right) \right]^{-1} \times \left[ \sum_{i=1}^{n} \left( \frac{l_i^2}{2D_i} \sum_{j=0}^{i-1} \frac{l_i}{D_j} \prod_{k=0}^{i-1} k_j \right) \right] \\
- \frac{l_i^2}{3D_i^2} \prod_{j=0}^{i-1} k_j \right] + \sum_{i=1}^{n} \left( \frac{l_i}{D_i} \prod_{j=0}^{i-1} k_j \right) \right] \times \left[ \sum_{i=1}^{n} \left( \frac{l_i}{D_i} \prod_{j=0}^{i-1} k_j \right) \right] \right]
\]

where \( D_i \) is the diffusion coefficient of the diffusant in the \( i \)th component layer, where \( i = 1, 2, \ldots n \), and is assumed to be independent of concentration, time, or positional coordinate; \( k_i \) is the distribution coefficient between the two layers, and \( l_i \) is the thickness of each layer. In our system, \( D_i \) and \( l_i \) are identical in each layer. This equation can be used to study the increase of time lag with membrane thickness. If we take \( k_i = 1 \), we are making the assumption that the gas concentrations at the interface between two adjacent films are equal, that is to say, there is no boundary layer between each pair of films. In that case, the time lags will be:

\[
\theta = \theta_1 \quad n = 1 \\
\theta = 4\theta_1 \quad n = 2 \\
\theta = 10\theta_1 + f_4(l_i, D_i, k_i) \quad n = 4 \\
\theta = 22\theta_1 + f_8(l_i, D_i, k_i) \quad n = 8 \\
\theta = 34\theta_1 + f_{12}(l_i, D_i, k_i) \quad n = 12
\]

where \( f_4(l_i, D_i, k_i) = 6\theta_1 \), \( f_8(l_i, D_i, k_i) = 42\theta_1 \) and \( f_{12}(l_i, D_i, k_i) = 110\theta_1 \). Accordingly the time lags are given by:

\[
\theta = \theta_1 \quad n = 1 \\
\theta = 4\theta_1 \quad n = 2 \\
\theta = 16\theta_1 \quad n = 4 \\
\theta = 64\theta_1 \quad n = 8 \\
\theta = 144\theta_1 \quad n = 12
\]

As it can be seen, the time lag is proportional to the

![Graph showing the variation of time lag values with the thickness of the membranes at different temperatures.](Image)
square number of films, it depends on $l^2$. Fig. 3 shows that the dependence of the time lag values on membrane thickness can be expressed satisfactorily by a second-order polynomial relation ($R^2 = 0.999$). The agreement between the model prediction and the time lag data, allows us to justify our assumption. Therefore, we can conclude that the variation in time lag with the number of films is due mainly to the increase of sample thickness, and the boundary layer effects between films can be considered negligible.

An attempt to quantify the effect on the gas diffusion of an air gap between films can be made in the two-layered membrane. We chose this sample for simplicity. This membrane may be treated as a composite of the type ABA, where A refers to LLDPE films and B to air gap. The experimental diffusion coefficient, $D_{ABA}$, for such a membrane will be given by $(2l_A + l_b)^2/60l_{ABA}$, while the diffusion coefficient of the membrane containing one film will be $D_A = l_A^2/60l_A$. The expression for $D_{ABA}$ is given by [5]

$$D_{ABA} = \frac{D_A}{2l_A} \left[ \left( \frac{4l_A}{D_A} + \frac{l_A}{D_{ABA}} \right) + \frac{l_A}{D_A} \left( \frac{l_A}{D_{ABA}} + \frac{l_A}{D_{ABA}} \right) \right] \left( \frac{2l_A}{D_A} + \frac{l_A}{D_{ABA}} \right).$$

As $D_B$ for the air gap is large compared with $D_A$ for the LLDPE film then

$$D_{ABA} \approx \frac{2l_A^2}{3D_A} + \frac{l_A l_B l_{ABA}}{2D_A s_A}$$

(6)

It follows that the relation between $\theta_1$ and $\theta_{ABA}$ can be written as:

$$\frac{\theta_{ABA}}{\theta_1} \approx 4 + \frac{3l_A s_B}{l_A s_A}$$

(7)

The first term on the right side is the same as it had been obtained without taking into account the effect of the air gap, and the second term arising from the existence of the gap between films. If the ratio $s_A/s_B$ is taken as the solubility of carbon dioxide in LLDPE, Eq. (7) can be used to evaluate the effect of the air gap on the time lag. In order to do this, the thickness of the gap may be estimated from data in Table 1. In this way, in the most unfavourable case, the difference between $\theta_{AA}$ and $\theta_{ABA}$ would be 9.8%. These facts support that the effect of an air gap between LLDPE films on the time lag would not be significant. Nevertheless, as the gap increases, its effect starts to be relevant. For example, if there was an air gap whose thickness was 15% of that of individual films, the difference between $\theta_{AA}$ and $\theta_{ABA}$ would be around 20%.

4. Conclusions

The study of permeation of carbon dioxide through multiple LLDPE films shows that the permeability coefficient does not exhibit a significant variation on the number of stacked films, whereas the time lag increases with increasing the thickness of the samples. The analysis of the gas flux at steady state conditions shows that the boundary effects at the interface between films do not exist in all studied cases. In addition, we observed that the gas diffusion model in multilayer systems is valid to predict the time lag values in multilayer LLDPE films. Definitely, the results discussed above suggest that the stacking of LLDPE films has not any effect on the permeation of carbon dioxide through them.

References