polymer communications

Infra-red study of diffusion of CO_2 in highly oriented polyethylene films

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The diffusion coefficient for CO_2 in both unoriented and highly drawn films of polyethylene has been measured using Fourier transform i.r. spectroscopy and the ratio of the solubilities has also been found. In addition, scanning i.r. spectroscopy has been used to characterize the degree of orientation of the CO_2 molecules in the films.

(Keywords: polyethylene; oriented; diffusion; i.r. spectroscopy; carbon dioxide; solubility)

Introduction

Research on the diffusion of gases through polymers is carried out for two main reasons. The first is to assess the commercial potential of the polymer for use as a gas barrier in packaging or as a permselective membrane. The second reason is that by using different permeants as probes information may be obtained about the structure of the polymer and about the interaction of the permeant molecules with it.

The majority of research on diffusion of gases through polymer films relies on dynamic flow rate or time lag techniques. These methods usually involve the detection of permeant molecules emerging from the film surface to measure the flow rate through the film and thus can only give indirect information about the interaction of the permeant and the polymer. It is the purpose of this communication to show that the use of i.r. spectroscopy enables the detection of CO_2 within polyethylene films and permits its concentration to be studied in either static or dynamic experiments. This has the advantage of allowing the relative solubility to be determined independently of the diffusion coefficient at specific gas pressures, of permitting observations on thicker samples than it is convenient to study by the conventional techniques and of permitting the observation of orientation of the CO_2 molecules in oriented films. It has the further advantage that there is no pressure drop across the sample at any stage in the measurements.

Dynamic measurements

Dynamic measurements have been made on an unoriented sample and three samples of highly oriented polyethylene (Hizex 7000-F) drawn at 115°C to draw ratios $\lambda = 6$, 13 and 19, starting from quenched isotropic sheets. Full experimental details of the preparation and structure of these oriented sheets have been given in a previous publication[1]. A Bomem 151 Fourier transform i.r. spectrometer was used with resolution of 2 cm^{-1}. The i.r. cell allowed CO_2 to pass over both faces of the sample and the output ports were open to the atmosphere. The cell was first purged with N_2 before introducing the CO_2 and the purge continued until no absorbed CO_2 was detectable. After the flow of CO_2 was established, spectra were run at regular intervals until the sample was saturated. This was the absorption run. The desorption run was similar, except that the polymer was first saturated with CO_2 and then a flow of N_2 was started to sweep away the desorbed CO_2. All measurements were made at 25 ± 1°C.

Only data in the spectral region 2150–2450 cm^{-1}, the region of the CO_2 antisymmetric stretching mode, have been analysed. In this region the spectra may be considered to consist of the background spectrum (due to cell windows and polymer sample), the spectrum of free CO_2 in the cell and the spectrum of the CO_2 absorbed in the polymer. Nitrogen has no effect in the spectral region concerned. The background spectrum was subtracted from the total spectrum to obtain the peak due to absorbed gas on top of the broad band due to free gas. The very different shapes of these two components allowed their contributions to be separated by using the absorbances at two wavenumbers (2334 and 2360 cm^{-1}). For the desorption runs this separation was necessary only for the first few spectra, after which only absorbed CO_2 was present.

The diffusion coefficients were obtained from the data for the absorption runs using the equation:

$$D = \lim(t \rightarrow 0)\{(l\pi^{0.5}/4)\mathrm{d}[M(t)/M(\infty)]/\mathrm{d}(t^{0.5})\}^2$$

where l is the thickness of the sample, t is time and $M(t)$ and $M(\infty)$ are the mass uptakes of gas at time t and infinity, respectively, which are proportional to the corresponding absorbance peak heights. A similar equation was used for the desorption runs. The values of D and the relative solubilities are shown in *Table 1*. The values of D are compared with those obtained by a mass spectrometer method, which will be reported elsewhere, in *Figure 1*.

Orientation study

This study was performed in a similar manner to the dynamic study, except that a Perkin-Elmer 580B ratio-recording i.r. spectrometer was employed, since

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only static measurements at effectively $t = \infty$ were made. Parallel polarizers were mounted in both sample and reference beams and the sample was rotated through 90° to obtain parallel and perpendicular spectra in the region 2150–2450 cm^{-1} with resolution of ~2.5 cm^{-1}. Since rather small changes of absorbance were to be detected, the observed spectra were least squares fitted to the spectra of free CO_2 and CO_2 dissolved in liquid paraffin and the required contribution of the latter spectrum was taken as a measure of the absorbance due to CO_2 dissolved in the sample, and hence its concentration (*Figure 2*).

Table 1 Draw ratio (λ), thickness (l), diffusion coefficient (D) and relative solubility (S_{rel}) of CO_2

λ	l ($\times 10^4$) (cm)	D ($\times 10^8$) ($cm^2 s^{-1}$)	S_{rel}
1	341.2 ± 2	16.8 ± 1.5	1
6.5 ± 0.2	124.9 ± 1.4	10.0 ± 0.4	0.786
12.9 ± 0.4	130.8 ± 0.3	1.21 ± 0.08	0.547
18.6 ± 0.5	89.4 ± 1.5	0.45 ± 0.03	0.459

Table 2 Orientation averages for CO_2

λ	$D_{i.r.}$	$\langle \cos^2 \theta \rangle$	$\langle P_2(\cos \theta) \rangle$
6.5 ± 0.2	1.244	0.384	0.075 ± 0.016
12.9 ± 0.4	1.332	0.400	0.100 ± 0.007
18.6 ± 0.5	1.368	0.406	0.109 ± 0.025

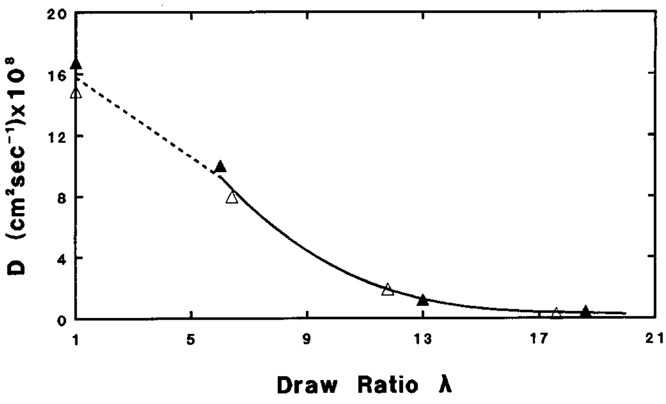

Figure 1 Comparison of diffusion coefficients from i.r. (▲) and mass (△) spectrometry

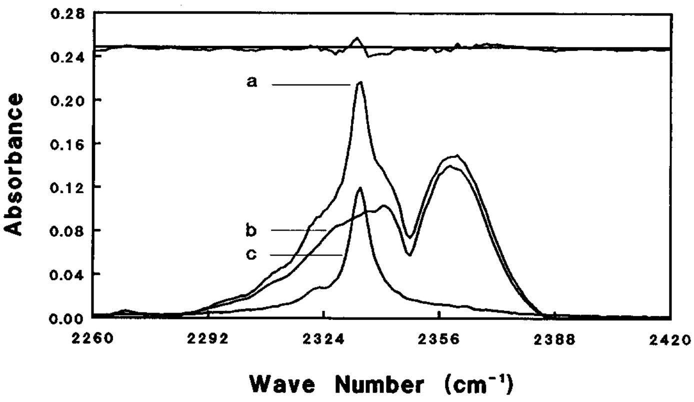

Figure 2 I.r. spectra of CO_2 dissolved in polyethylene: (a) dissolved gas plus free gas surrounding sample; (b) gaseous CO_2; (c) CO_2 dissolved in liquid paraffin. Top curve shows deviation from (a) of a best fit of a combination of (b) and (c) to (a)

The absorbances A_π and A_σ for the parallel and perpendicularly polarized spectra were used to calculate the values of $\langle \cos^2 \theta \rangle$ and $\langle P_2(\cos \theta) \rangle$, where θ is the angle between the long axis of the CO_2 molecule and the draw direction of the polymer, using the expressions:

$$\langle \cos^2 \theta \rangle = D_{i.r.}/(D_{i.r.} + 2)$$

$$\langle P_2(\cos \theta) \rangle = (D_{i.r.} - 1)/(D_{i.r.} + 2)$$

where $D_{i.r.} = A_\pi / A_\sigma$ is the dichroic ratio. The values found are shown in *Table 2*.

Discussion and conclusions

It is clear that a study of the i.r. spectrum of CO_2 molecules absorbed in oriented polymers can give useful information not only about the solubility and diffusion coefficients but also about more subtle aspects of the interaction of the gas molecules with the polymer. Previous work on samples of polyethylene with λ up to ~6 has shown a similar degree of orientation of dissolved CO_2 molecules to that observed here[2]. The present results suggest, but do not confirm, that there may be a small increase in the degree of orientation at higher λ. That the effect of higher λ on the orientation of the CO_2 molecules is so small is somewhat surprising at first, since the solubilities, and more particularly the diffusion coefficients, are still quite sensitive to draw ratio above $\lambda = 6$. This suggests that the CO_2 molecules are not only excluded from the crystalline regions of the polymer, but also from the more ordered non-crystalline regions.

Future work will involve studies of solubility and orientation of CO_2 in other polymers, including those expected to show dual mode sorption, where it will be important to study the effects of pressure on sorption and diffusion.

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