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Influence of the crystallinity on the transport properties of polyethylene

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Transport properties of dichloromethane were analysed in high- and low-density polyethylene films, obtained with different thermal treatments, in order to correlate sorption and diffusion with the crystallinity of the samples. The crystalline fraction of all the analysed samples was evaluated from density and X-ray data; it ranged from 40%–85%. From the X-ray diffractograms the reciprocal of the width at half-height for the strongest reflection was derived for all the samples; it was considered as an order parameter. It was found that the sorption depends only on the fraction of amorphous phase; in fact, the specific sorption, normalized for the crystallinity of the sample, is constant for all the samples. However, the zero concentration diffusion coefficient, D_0, varies with the sample crystallinity, but there is no simple correlation between these two parameters; rather a transition seems to separate two ranges in which the diffusion coefficient decreases with the crystallinity. At variance, a linear decrease of the diffusion parameter with the order parameter, derived from the X-ray diffractograms, was found in the whole range of crystallinity.

1. Introduction

In a semicrystalline polymer, the crystalline regions are generally impermeable to the vapour penetrants [1–4]. In fact, in many investigated systems, the X-ray spacings are not altered by the sorption process. Therefore, in samples of different crystallinities, the solubility is directly proportional to the amorphous fraction

$$S = S_a X_a = S_a(1 - X_c) \quad (1)$$

where X_a is the volume or the mass fraction of the amorphous component and X_c the crystallinity. This was confirmed for the sorption of different vapours and gases in polyethylene samples of different densities [5–7]. Besides the reduction of sorption, the presence of impermeable crystallites lowers the overall rate of transport. However, the value of the diffusion coefficient is not directly proportional to the amorphous content, but shows a more complex dependence on it. The decrease of the diffusion coefficient is due to a more tortuous path for the penetrant molecules that must bypass the impermeable obstacles. A number of expressions have been deduced in analogy to the disruption of current flow through a medium containing particles with a dielectric constant of nearly zero. In particular, the following expression has been suggested

$$D = D_a/\tau \quad (2)$$

where τ is the tortuosity factor, which depends not only on the degree of crystallinity but also on the size, shape and distribution of crystallites. Estimation of τ from a knowledge of the geometry of a two-phase system is not possible, and it must be experimentally measured.

For the diffusion of certain permanent gases through various polyethylenes, Michaels and Bixler [8] found that τ increased in line with the equation

$$\tau = X_a^{-n} \quad (3)$$

where the parameter n is presumably characteristic of both the polymer and its processing conditions, and was found to be 1.25 for branched polyethylene and 1.88 for linear high-density polyethylene.

In this work we analysed the transport of dichloromethane vapour in different polyethylene samples, ranging in mass crystallinity from 40% to about 85%. The different samples were analysed with different techniques in order to find a correlation between crystallinity and transport properties of a small and interacting molecule such as dichloromethane, already used in many structural studies [9–12].

2. Experimental procedure

Low-density polyethylene (LDPE) of $M_n = 24\,000$ and $M_w = 215\,000$ and high-density polyethylene (HDPE) of $M_n = 8000$ and $M_w = 92\,000$ were kindly supplied by RAPRA (UK).

The films were obtained by heating the PE pellets at a temperature above the melting point, pressing them into a film shape of thickness 0.015–0.020 cm, and cooling them in ice–water (samples LDPE-Q and HDPE-Q, respectively) or slow cooling at 2 °C min^{-1} (samples LDPE-C and HDPE-C, respectively). Samples LDPE-Q and HDPE-Q were annealed at 110 and

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125 °C, respectively, for 24 h (samples LDPE-A and HDPE-A).

The density was measured at 25 °C by floating the sample in a mixture of methyl carbitol and buthyl cellosolve.

The transport properties, sorption and diffusion, were measured by a microgravimetric method, using a quartz spring balance, having an extension of 20 mm mg^{-1}. The penetrant used was dichloromethane and the experiments were conducted at a temperature of 25 °C. Sorption was measured as a function of vapour activity, $a = p/p_T$, where p is the actual pressure to which the sample was exposed and p_T is the saturation pressure at the temperature of the experiment. The samples were tested 1 day after preparation or annealing.

Wide-angle X-ray diffractograms (WAXD) were obtained by using a PW 1050 Philips powder diffractometer ($\text{Cu}K_\alpha$ + nickel-filtered radiation). The scan rate was $2°\theta\ \text{min}^{-1}$.

3. Results and discussion

The diffractograms of sample LDPE-Q are given in Fig. 1 and show the shape usually reported in the literature for polyethylene. From the diffractograms of all the samples, the X-ray crystallinity was derived for each sample, by comparing the area under the crystalline peaks (subtracting the amorphous contribution) and the total area. The X-ray crystallinities, X_1, are reported in Table I for all the analysed samples.

In addition to the crystallinity, the reciprocal of the width at half-height, A, for the polyethylene strongest reflection ($2\theta = 21.5°$), can be used as an index of the order level attained by the samples crystallized in different conditions. In fact, for a powder composed of relatively perfect crystalline particles, the mean crystallite size, L, can be determined by the well-known Scherrer equation, in which L is inversely related to the width at half-height of the reflection [13]. However, for imperfect crystals, the intensity profile is also affected by lattice distorsions; therefore, we prefer to use the $1/A$ parameter as an index of order instead of the crystal thickness, L. This parameter, evaluated as schematically represented in Fig. 1, is reported in Table I for all the samples.

The mass crystallinity was derived from the measured density, d (g cm^{-3}), under the assumption that the crystalline and amorphous components have ideal values of density for the perfect crystal ($d_c = 1.000$ g cm^{-3}), and fully relaxed supercooled melt ($d_a = 0.853$ g cm^{-3}), according to the relation

$$X_c = d_c(d - d_a)/d(d_c - d_a) \qquad (4)$$

The crystallinities calculated from the density values, X_2, are reported in Table I.

A comparison between the crystallinities calculated with the two different methods, shows that the density method slightly overestimates the value of crystallinity, with respect to the X-ray method, particularly for the lower crystallinity samples. This could be due to the density of the amorphous phase being higher than that of a fully relaxed supercooled melt. In fact, the amorphous chains, connected with the crystalline lamellae, surely have a higher density than a true amorphous phase and, therefore, they increase the value of the bulk density. Nevertheless, the values are very near and we can consider a mean value of crystallinity, for the evaluation of the transport properties as a function of the crystallinity. The mean values, X_c, are also reported in Table I for all the samples.

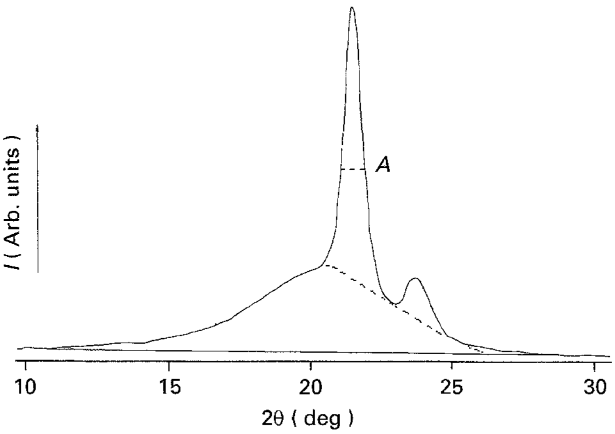

Figure 1 Wide-angle X-ray diffractogram of sample LDPE-Q.

TABLE I The crystallinity, X_1, derived from X-ray diffractograms, crystallinity, X_2, derived from density data, average crystallinity, X_c, and the order parameter $1/A$ for all the investigated samples

Sample	X_1	X_2	X_c	$1/A(\text{deg } 2\theta)^{-1}$
LDPE-Q	0.38	0.42	0.40	1.2
HDPE-Q	0.64	0.66	0.65	1.8
LDPE-C	0.46	0.49	0.48	1.3
HDPE-C	0.64	0.67	0.65	1.8
LDPE-A	0.48	0.52	0.50	1.3
HDPE-A	0.82	0.84	0.83	2.0

In the case of high-density polyethylene, the quenched (HDPE-Q) and the slowly cooled sample (HDPE-C) show the same crystallinity and $1/A$ parameter: the rate of crystallization is so high that different conditions are unable to produce different crystallinities; instead, in the low-density sample, the slow cooling process produces a more crystalline sample (LDPE-C) : in this case the annealing process of the quenched sample does not increase the crystallinity with respect to the slowly cooled sample. Therefore, the transport properties were measured for the four samples with different crystallinities.

Fig. 2 shows the equilibrium concentration of sorbed dichloromethane, as a function of the vapour activity, for all the samples. We observe that, as expected, the sorption decreases as the crystallinity increases. If the specific sorption, that is the sorption of the amorphous phase, is constant, we must have in all the samples

$$C_{sp} = C_a/X_a \qquad (5)$$

where C_a is the sorption, at a given activity, of a sample with an amorphous fraction $X_a = 1 - X_c$.

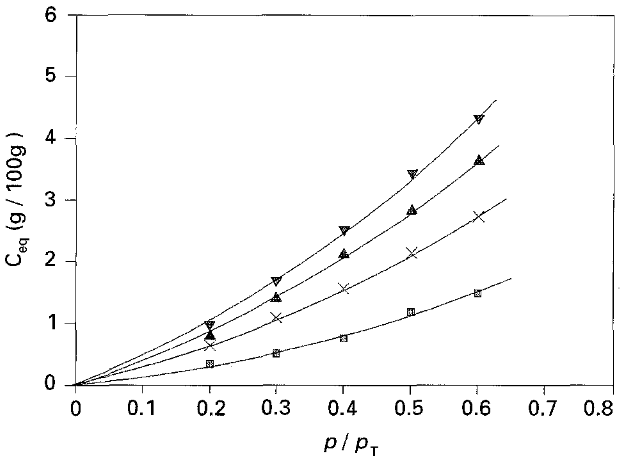

Figure 2 The equilibrium concentration of dichloromethane, c_{eq}, as a function of vapour activity $a = p/p_T$, for samples (△) LDPE-Q, (×) HDPE-Q, (▲) LDPE-A and (□) HDPE-A.

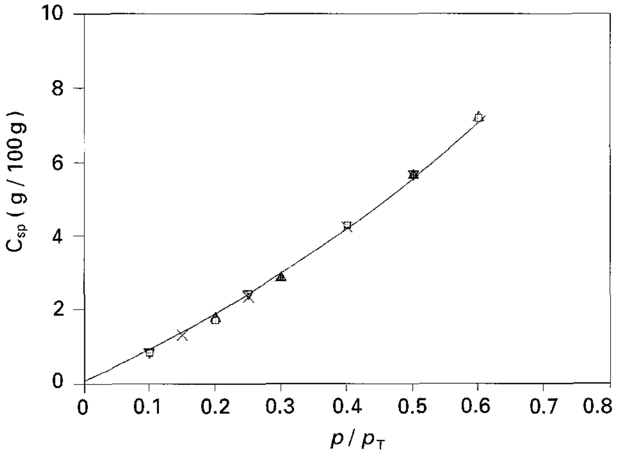

Figure 3 The specific sorption, c_{sp}, as a function of vapour activity, for samples (△) LDPE-Q, (×) HDPE-Q, (▲) LDPE-A, and (□) HDPE-A.

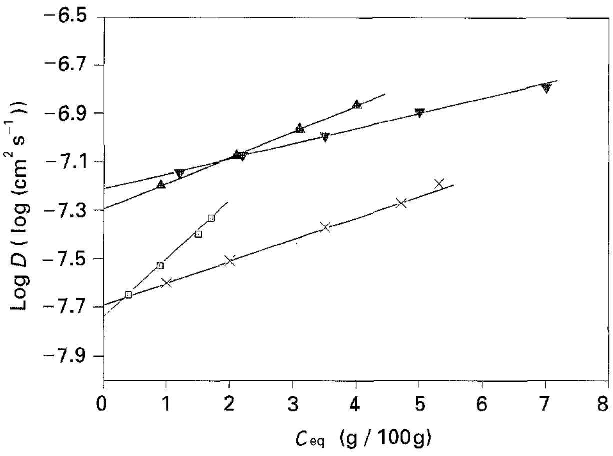

Figure 4 The logarithm of the diffusion coefficient, D, as a function of the equilibrium concentration, for samples (△) LDPE-Q, (×) HDPE-Q, (▲) LDPE-A, and (□) HDPE-A.

TABLE II The zero concentration diffusion coefficient D_0 (cm^2 s^{-1}) and the concentration coefficient, γ, for the investigated samples

Sample	$D_0(\times 10^8)$	γ
LDPEQ	6.0	14
LDPEA	5.0	21
HDPEQ	2.0	26
HDPEA	1.8	61

Fig. 3 shows C_{sp}, calculated using the mean value of crystallinity of the samples, as a function of activity. All the experimental points fit the same curve, showing that the specific sorption of dichloromethane in samples of polyethylene, varying in crystallinity from 40%–83%, is constant at each vapour activity, and therefore independent of the fractional free volume. This parameter, in fact, ought to be different in samples of different crystallinity. At each vapour activity, the sorption was reported as c_t/c_{eq}, where c_t is the concentration of vapour at time t, and c_{eq} the equilibrium value, as a function of square root of time, $t^{1/2}$. From the initial linear part of the Fickian curves it was possible to derive a diffusion coefficient, $\bar{D}$ (cm^2 s^{-1}), from the relation

$$c_t/c_{eq} = 4/d(Dt/\pi)^{1/2} \qquad (6)$$

where d is the thickness (cm) of the sample.

The diffusion parameter is not constant at each vapour activity, but increases with increasing vapour concentration; it is, therefore, important to determine the dependence of diffusion on concentration, in order to extrapolate to zero penetrant concentration and obtain the thermodynamic parameter, D_0, which is related to the fractional free volume. Generally, the dependence is of the exponential form

$$D = D_0 \exp(\gamma c) \qquad (7)$$

where γ is the concentration coefficient, also related to the fractional free volume and to the effectiveness with which the penetrant plasticizes the polymer.

Fig. 4 shows the logarithm of the diffusion coefficient as a function of the equilibrium concentration, for all the samples. We observe different straight lines, giving different extrapolated diffusion coefficients, D_0(cm^2 s^{-1}), and a different dependence of diffusion on concentration, too.

The derived values of D_0 and γ for each sample are reported in Table II. As expected, the fractional free volume shows its biggest influence on the diffusion parameter, which is exponentially related to it [2], through the relation

$$D_0 = \exp(-A/f) \qquad (8)$$

In Fig. 5 the logarithm of the D_0 value is reported as a function of the mean crystallinity of the samples. Although we have only four different values, it seems that there is no simple relationship correlating the diffusion parameters with the crystallinity of the samples. Rather, a transition between 50% and 60% crystallinity separates a decrease in this parameter in two different ranges of crystallinity.

Fig. 6 shows the concentration coefficient, γ, as a function of crystallinity of the samples. In this case

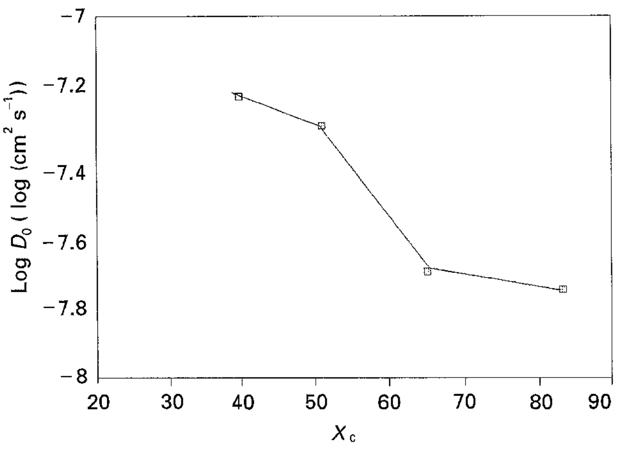

Figure 5 The logarithm of the zero concentration diffusion coefficient, D_0, as a function of the crystallinity of the samples.

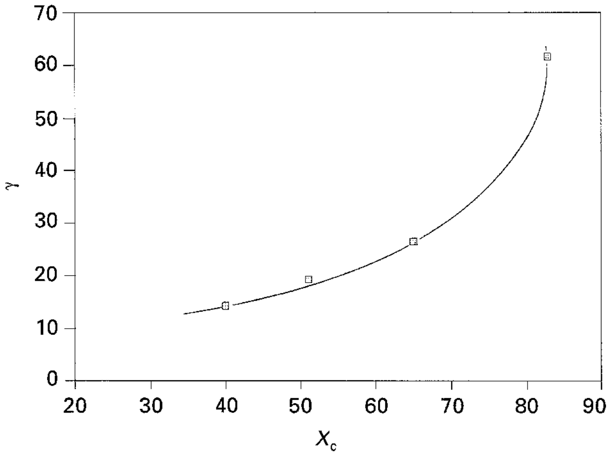

Figure 6 The concentration coefficient, γ, as a function of the crystallinity of the samples.

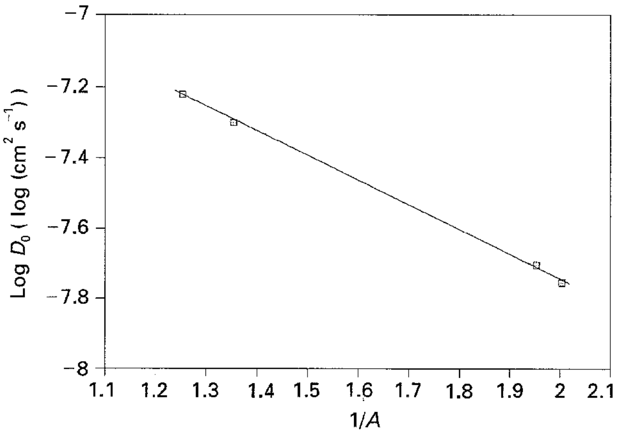

Figure 7 The logarithm of the zero concentration diffusion coefficient, D_0, as a function of the order parameter $1/A$.

a linear increase of the coefficient is observed up to a crystallinity of 65%, whereas a steeper increase occurs for the most crystalline sample.

In Fig. 7 the logarithm of the diffusion values are reported as a function of the order parameter $1/A$, which is related to the crystalline dimensions. We observe a good linear dependence of the diffusion on this parameter, showing that the tortuosity increases on increasing the crystalline dimensions.

4. Conclusion

We have analysed samples of low- and high-density polyethylene, of varying crystallinity, and characterized by different order parameters, derived from the X-ray diffractograms.

The two generally used techniques for determining the crystallinity, i.e. density and X-rays, give a good agreement for this parameter in all the samples.

The transport properties, sorption and diffusion, were measured and correlated with the crystallinity of the samples. The sorption is influenced only because the increase of the crystallinity reduces the permeable phase; the specific sorption, that is the sorption normalized by the amorphous fraction, is the same for all the samples, in spite of a reduced free volume with increasing crystallinity. We can therefore conclude that, in the range of crystallinity 40%–85%, the thermodynamic parameter, S, at low vapour activity, is not influenced by the free volume and by the fraction of the amorphous tie molecules connecting the crystalline blocks.

At variance, the zero concentration diffusion parameter, D_0, as expected, is not constant but varies with the crystallinity. No simple relation was found between diffusion and crystallinity of the samples; rather a transition is observed, separating the behaviour of samples with crysallinity below 60% and above this figure. Instead, a simple linear relation was found between the logarithm of the diffusion parameters and the order parameters $1/A$ derived from the X-ray diffractograms, which is correlated with the crystalline dimensions. This result is too limited to be used for a general picture, but it could constitute a basis for future experimental investigations on different systems. Unfortunately, it is difficult, if not impossible, to change the crystalline dimensions, without simultaneously changing the overall crystallinity of the sample, and vice versa; therefore, the two effects, crystallinity and crystal dimensions, cannot be separated and both must be taken into account.

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