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Influence of the crystallinity on the transport properties of isotactic polypropylene

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Abstract

Samples of polypropylene of varying crystallinity were obtained by blending isotactic with atactic polypropylene, and the crystallinity determined by X-ray diffraction and differential scanning calorimetry. Crystallinity ranged between 20 and 75%. The transport properties of dichloromethane were analysed varying the activity of the vapour. We observed that the sorption decreases, as the crystallinity increases, proportionally to the decrease of the amorphous fraction. As matter of the fact, the specific sorption, normalized by the amorphous fraction, does not depend on the crystallinity. At variance, a simple correlation between the thermodynamic diffusion coefficient and the crystallinity was not obtained; at low values of this parameter, up to 40%, the zero concentration diffusion coefficient is independent of it. A sharp transition separates a range of crystallinities, in which the diffusion parameter decreases, increasing the crystallinity, due to the tortuosity of the path, and shows that the presence of the impermeable crystals is important only for values higher than 50%. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The study of the influence of crystallinity and orientation on the transport properties of gases and vapours in polymeric films is very important both theoretically and technologically [1–4]. Sorption and diffusion determine the permeability of a film, and this parameter is of fundamental importance if the film has to be used as packaging material. The food packaging industry needs particular performances of the materials selected, particularly in terms of the barrier requirements [5–10]. Both crystallinity and molecular orientation generally decrease the permeability, due to decreased sorption and/or diffusion. In most cases the crystalline regions were found impermeable to the vapour penetrants [1–4]. Therefore in samples of different crystallinities, the solubility, S_a g/g, is directly proportional to the amorphous fraction

$$S = S_a X_a = S_a(1 - X_c) \tag{1}$$

where X_a is the volume or the mass fraction of the amorphous component, and X_c the crystallinity of a bi-phase system. The evaluation of the sorption is more complex in systems in which liquid-crystalline phases or mesophases are present. They were, in fact, found impermeable to the vapours, at least at low activity; therefore their presence has to be recognised and quantitatively evaluated [11,12].

Besides the reduction of sorption, the presence of impermeable crystallites can lower the overall rate of transport, 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:

$$D_0 = D_a/\tau \tag{2}$$

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.

In the case of polyethylene, it was found that D_0 varies with crystallinity, but there is no simple relation between these two parameters; rather a transition seems to separate two ranges in which the diffusion coefficient decreases with the crystallinity [13].

Isotactic polypropylene (iPP) is one of the most used polymers for packaging applications [14]. When iPP is quenched from the melt to low temperatures, it forms a phase of intermediate order between the amorphous and

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the crystalline phase, called "smectic polypropylene" [15]. Quenching at intermediate temperatures, three-phase smectic–monoclinic–amorphous systems are obtained. In these systems it was found a constant fraction of amorphous phase and a higher monoclinic content on increasing the quenching temperature [16]. Therefore it is not easy to obtain two-phase systems with different amorphous fractions, in order to investigate the change of transport properties with crystallinity.

On the contrary, atactic polypropylene (aPP) was found to be miscible with iPP in the melt, and, in the solidified melt, is located mainly inside the spherulites of the isotactic polypropylene, on a scale approximately equal to that of the crystalline lamellae [17]. It is therefore possible to vary the crystallinity of iPP, by blending with aPP, thus obtaining a single amorphous phase.

In this paper we analysed the transport of dichloromethane vapour in blends of aPP–iPP, ranging in mass crystallinity from 20 to 75%.

The different samples were analysed with different techniques in order to find a correct value of crystallinity and a correlation between crystallinity and transport properties. A small interacting molecule such as dichloromethane, already used as a model molecule in many structural studies, was utilised.

2. Experimental

Isotactic polypropylene of $M_n = 15,600$ and $M_w = 307,000$ was kindly supplied by RAPRA (UK). Atactic polypropylene was synthesised by the group of Prof. Zambelli (University of Salerno).

Blends of iPP and aPP were prepared by co-dissolving the proper weight of the polymers in *p*-xylene at high temperature and then precipitating with methanol. The precipitate was vacuum dried at 70°C for two days to ensure the complete removal of the solvent. Films of the pure iPP and of the blends were obtained by heating the powders at 180°C, pressing them into a film shape of thickness 0.15–0.20 mm, and quenching them into an ice-water bath. The atactic polymer was heated at 80°C and quenched in the same bath. Isotactic polypropylene was also melted in the press and crystallised at 100°C.

The sample codes are as follows:

iPP crystallised at 100°C (Sample C100)
iPP annealed at 155°C for 24 h (Sample A155)
Blend of 80% in weight of iPP and 20% of aPP (Sample B80–20)
Blend of 50% in weight of iPP and 50% of aPP (Sample B50–50)
Blend of 20% in weight of iPP and 80% of aPP (Sample B20–80)
aPP quenched (AQ)

Wide-angle X-ray diffractograms (WAXD) were obtained using a Philips PW 1710 Powder diffractometer (CuKα–Ni filtered radiation). The scan rate was 2°θ/min.

Differential scanning calorimetry (DSC) was carried out over the temperature range −70 to 250°C, using a Mettler TC11 DSC purged with nitrogen and chilled with liquid nitrogen. Runs were conducted at a heating rate of 20°C/min.

The transport properties were measured by a microgravimetric method, using a quartz spring balance having an extension of 18 mm/mg. The penetrant used was dichloromethane and the experiments were conducted at 25°C. Sorption was measured as a function of vapour activity, $a = p/p_0$, where p is the actual pressure to which the sample was exposed and p_0 the saturation pressure at the temperature of the experiment.

3. Results

3.1. Crystallinity of the samples

The crystallinity of all the samples was derived by WAXD and calorimetric curves by DSC.

In Fig. 1 the WAXDs of samples B80–20 and B20–80 are reported. The first is representative of all the other crystalline samples (B50–50, C100 and A155), whereas the second is reported because it only presents a disordered monoclinic form. The WAXD of sample B80–20 shows the crystalline peaks of the monoclinic α form of isotactic polypropylene, with the peaks at 14.1, 16.8, 18.4, 21.2 and 24° of 2θ. At variance, in the diffractogram of sample B20–80 the intensity of the iPP peaks at 14.1 and 16.8° of 2θ is inverted, indicating a more disordered and less crystalline monoclinic form. From the diffractogram it is possible to derive the fraction of crystalline phase, dividing the area of the crystalline peaks by the total area. The diffractogram

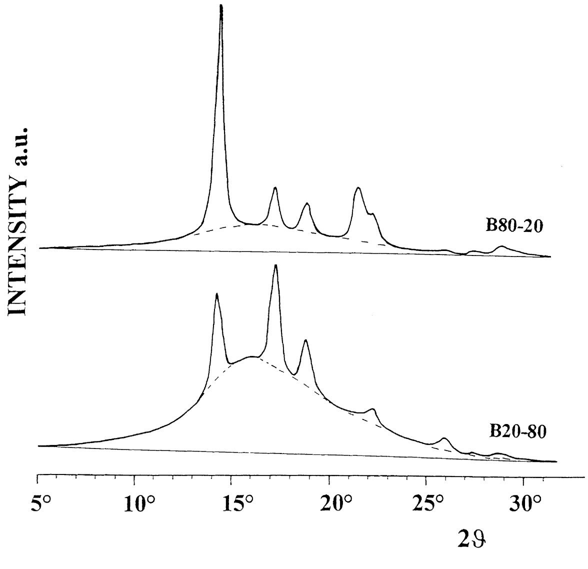

Fig. 1. Wide-angle X-ray diffractograms of samples B80–20 and B20–80.

Table 1
The calculated values of crystallinity

Sample	X_c% (RX)	X_c% (DSC)	D_0 (cm^2/s)
AQ	–	–	9.78×10^{-9}
B20–80	20	18	9.50×10^{-9}
B50–50	38	34	9.50×10^{-9}
B80–20	55	52	4.25×10^{-9}
C100	60	58	2.10×10^{-9}
A155	75	70	1.4×10^{-9}

of the amorphous phase was drawn over the baseline, with its maximum at 15.8° of 2θ, as shown in the figure [15]. The calculated values of crystallinity for all the samples are reported in Table 1.

Beside the derivation of the crystallinity, it is worth noting that the quenched samples do not show any evidence of the smectic phase. In fact, when pure iPP is quenched in the same conditions of the present films, it always shows the presence of an intermediate form, between the crystalline and amorphous one, called smectic polypropylene. At variance, even with the lowest fraction of iPP (sample B20–80), the quenched sample results in crystallinity, although characterised by low crystallinity, as evident from the inverted relative intensity between the peaks at 14.2 and 16.8° of 2θ.

In Fig. 2 we report the calorimetric curves of samples B20–80 and B80–20, as representative of all the others. In the less crystalline B20–80 sample, the glass transition is well evident at -5°C, and the melting peak appears at 162°C. Also from DSC, no evidence of smectic phase is observed, in all the samples. The values of crystallinity, obtained by normalising ΔH_m by the value of $\Delta H_0 = 165$ J/g [19] are reported in Table 1. The comparison with the values of crystallinity obtained by the X-ray diffractograms, shows that the calorimetric values are slightly lower than the others; in contrast their values depend on the chosen ΔH_0. In any case, they are very near, and we used the values of crystallinity obtained by X-ray diffraction.

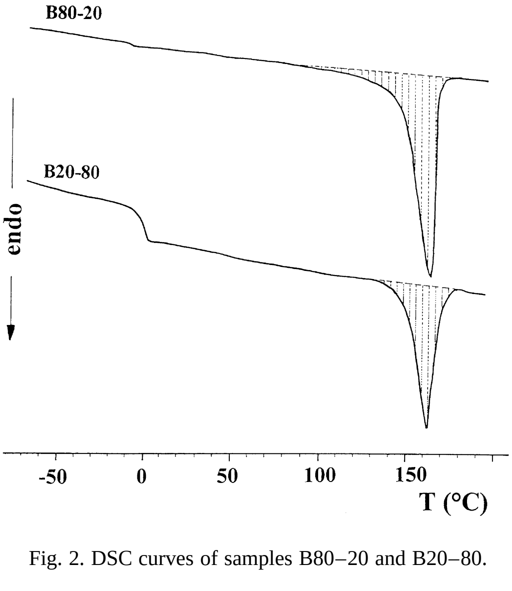

Fig. 2. DSC curves of samples B80–20 and B20–80.

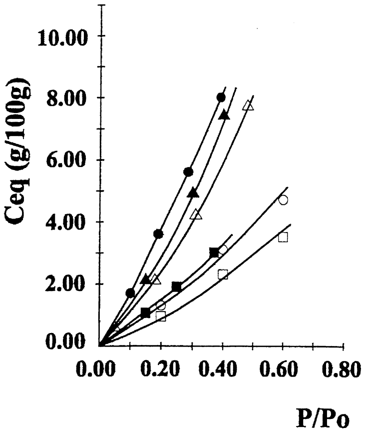

Fig. 3. The equilibrium concentration of dichloromethane vapour, as a function of activity, for samples C100 (○), A155 (□), B80–20 (■), B50–50 (△), B20–80 (▲), AQ (●).

3.2. Transport properties

In Fig. 3 we report 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

$$C_{sp} = C_{eq}/X_a$$

where C_{eq} is the sorption, at a given activity, of a sample with an amorphous fraction $X_a = (1 - X_c)$.

Fig. 4 shows C_{sp} calculated using the X-ray 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 polypropylene, varying in crystallinity from 20 to 75%, is constant, as already found for polyethylene. The constant

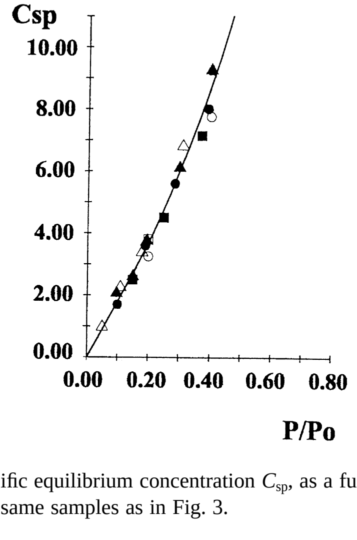

Fig. 4. The specific equilibrium concentration C_{sp}, as a function of vapour activity, for the same samples as in Fig. 3.

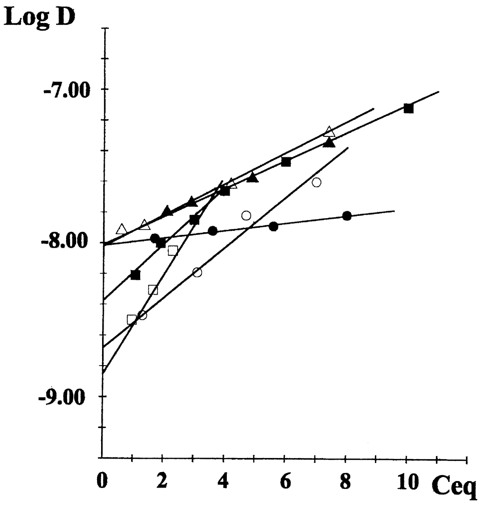

Fig. 5. The logarithm of the diffusion coefficient, as a function of equilibrium concentration, for the same samples as in Fig. 3.

value of the specific sorption both for aPP and iPP indicates that the two forms of polypropylene have the same interaction with the vapour, and the same transport properties.

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, $t^{1/2}$.

All the curves were linear in the initial part; in this case the curves are Fickian and it is possible to derive a diffusion coefficient, D (cm^2/s) from the relation:

$$C_t/C_{eq} = \frac{4}{d}\left(\frac{D\cdot t}{\pi}\right)^{1/2}$$

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

Since the diffusion coefficient increases with increasing concentration, we have 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 and to the tortuosity of the path, due to the impermeable crystalline phase. Generally the dependence is of the exponential form:

$$D = D_0 \exp(\gamma C_{eq})$$

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

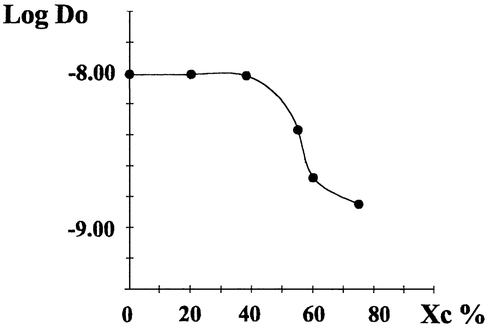

Fig. 6. The logarithm of the D_0 parameter as a function of the crystallinity of the samples.

Fig. 5 shows the logarithm of the diffusion coefficient as a function of the equilibrium concentration, for all the samples. We observe that the amorphous aPP sample, and the less crystalline samples B20–80 ($X_c = 0.20$) and B50–50 ($X_c = 0.38$) give the same extrapolated D_0 coefficients, but different dependence of diffusion on concentration, that is different γ coefficients. At variance, in sample B80–20, with a crystallinity of 55%, two ranges appear, in which the diffusion coefficients show a different dependence on concentration: at low vapour activity, and therefore at low concentration, the dependence is steeper than in the previous cases, and a different D_0 coefficient was extrapolated. After activity $a = 0.4$ we observe a lower dependence, and the experimental points fit the same curve as sample B20–80.

The more crystalline samples C100 ($X_c = 0.6$) and A155 ($X_c = 0.75$) show lower diffusion values, extrapolating to a lower D_0, and higher concentration coefficients.

The derived values of D_0 for each sample are reported in Table 1.

In Fig. 6 we report the logarithm of the zero diffusion coefficient as a function of the crystallinity of the samples. We observe an independence of D_0, up to crystallinity of 40%, a transition, between 50 and 60%, and a linear dependence at higher values of crystallinity.

4. Discussion

The results of the variation of the transport properties with crystallinity, presented here, are not easily interpretable. We must recall that we obtained samples of varying crystallinity by mixing iPP and aPP, and only samples C100 and A155 are composed of a homogeneous polymer. Therefore in all the other samples, the amorphous phase is composed by both atactic and the non-crystallised part of isotactic chains. The results of sorption show that the amorphous phase behaves as a homogeneous phase, and similarly in all the samples; as a matter of the fact we obtain a single sorption curve if we normalise the equilibrium concentration at each activity by the amorphous fraction derived by X-ray diffraction. At variance the results of diffusion show that the amorphous phase has the same zero concentration diffusion coefficient up to a fraction of 50% of crystallinity; thereafter we observe a very sharp decrease between 50 and 55%, and then a slower decrease of diffusion on the crystalline fraction. Before the transition we can infer that the amorphous matrix maintains the same properties, not influenced by the presence of impermeable crystals. Therefore the concept of tortuosity of the path, for the travelling penetrant molecules is not to be introduced up to crystallinity of 50%. Instead, when crystallinity is higher than 60% we can invoke the tortuosity of the path to explain the decrease of diffusion increasing the crystallinity.

More subtle is the explanation of the observed sharp transition between the two zones (up to 40% and over 60%). It is worth remembering that for iPP it a double glass transition was suggested, due to the presence of different types of amorphous material. Boyer [18,19], analysing many experimental results on the thermal expansion and mechanical loss data, hypothesised the presence of two glass-like transitions, the lower T_g(L) due to a relaxed and random coil amorphous phase, and the upper T_g(U) due to the fraction of amorphous phase disturbed by the crystals. The transition in the diffusion coefficient could mean that the amorphous matrix through which the passage of the vapour molecules occurs, changes from that corresponding to a more random amorphous component, having a lower T_g to that corresponding to a more constrained phase, characterised by the upper T_g. At high crystallinities this fraction becomes prevalent with respect to the other. This suggestion is quite reasonable, since, increasing the fraction of crystals, an increasing number of amorphous chains are in contact with them. These amorphous chains ought to have a lower fractional free volume and it is reasonable to observe a lower D_0 coefficient. Still increasing the crystallinity, the impermeable crystals continue acting as obstacles on the diffusion path, making it increasingly tortuous. Therefore the diffusion coefficient continues decreasing after the transition, being represented by the relation:

$$D_0 = D_a/\tau$$

where D_a is the coefficient not influenced by the tortuosity.

In our case, the extrapolation of the D parameter to zero crystallinity would give just the D_0 parameter of aPP, i.e. 9.5×10^{-9} cm^2/s.

5. Conclusions

We have analysed samples of iPP of varying crystallinity, using a blending procedure with aPP.

Analysing the transport properties, sorption and diffusion of dichloromethane vapour, we observed that, as far as the sorption is considered, all the samples behave ideally, i.e. the specific sorption does not depend on the crystallinity. All the samples fit the vapour-concentration–activity curve.

At variance, a simple equation representing the dependence of the thermodynamic diffusion parameter was not found. A sharp transition separates the two zones: at low crystallinity D_0 is independent of this parameter; the amorphous matrix represents the largest part of the sample and the vapour molecules pass without being disturbed by the crystals. The second zone appears after crystallinity of 60%; in this case the amorphous part is the smaller part of the sample, and it is mainly disturbed by the presence of the crystals, so that the tortuosity of the path also becomes relevant. The fact that the extrapolated value of D_0 to zero crystallinity, gives the same D_0 as the atactic sample, is a strong evidence for this suggestion.

Acknowledgements

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