ELSEVIER

Polymer 42 (2001) 953–962

polymer

www.elsevier.nl/locate/polymer

Blends of bacterial poly(3-hydroxybutyrate) with synthetic poly(3-hydroxybutyrate) and poly(epichlorohydrin): transport properties of carbon dioxide and water vapour

O. Miguel, J.L. Egiburu, J.J. Iruin*

Polymer Science and Technology Department and Institute for Polymer Materials (POLYMAT), University of the Basque Country, P.O. Box 1072, 20080 San Sebastian, Spain

Received 12 January 2000; received in revised form 26 May 2000; accepted 12 June 2000

Abstract

The water vapour and carbon dioxide transport properties have been measured of bacterial (isotactic) poly(3-hydroxybutyrate) (iPHB) and its blends with synthetic (atactic) PHB (aPHB) and poly(epichlorohydrin) (PECH) have been measured. The purpose of this work is to study the transport properties of iPHB blends with a miscible second polymer, intended as a polymeric toughener that does not impair the original iPHB biodegradability. Thus, only iPHB rich blends containing up to 40% of aPHB or PECH were considered. The effect of aPHB on the blends is to increase the sorption and permeability with respect to pure iPHB due to the reduction in the level of crystallinity, while PECH tends to decrease the water and carbon dioxide solubilities of the blend. The blends have essentially the same permeability to CO_2, although the water transmission rates are lower for the iPHB/PECH system. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3-hydroxybutyrate); Miscible blends; Transport properties

1. Introduction

Poly(hydroxyalkanoates), PHA, comprise a family of biopolymers that has attracted much attention recently, due to their full biodegradability, biocompatibility and natural origin. Several applications have been proposed for these polymers in the fields of medicine, agriculture, and packaging [1–3].

The most studied and easily produced member of this family is poly(3-hydroxybutyrate), iPHB, an isotactic, high molecular weight polymer with a melting point around 172°C, and a glass transition close to 0°C. Produced in the form of intracellular granules by several microorganisms, iPHB serves as a carbon and energy storage material. However, some drawbacks have prevented its introduction in the market as a valid alternative to the currently widespread non-degradable oil-based thermoplastics. Some of these drawbacks are its fragility, thermal degradability at temperatures not far above the melting point, and its high price [4].

Among the various strategies developed over the years to improve the properties of iPHB, we shall mention two of them, namely copolymerization and blending. Several kinds of PHA copolymers have been described in the literature incorporating structural units such as 3-hydroxyvalerate, 4-hydroxybutyrate, or 3-hydroxyhexanoate [5]. These materials are intended to show an increased toughness by incorporating flexible units in the polymeric chain, as well as to improve the processability via the reduction of the melting temperature, so minimising the risk of thermal degradation.

The other main alternative to achieve these goals is blending with other polymers, both biodegradable and nonbiodegradable. Although many immiscible iPHB based blends have been described in the literature[6], it seems that little or no improvement in the physical properties is achieved in these cases, due to the incompatibility between iPHB and the second component. Some polymers that form immiscible blends with iPHB are ethylene–propylene rubber, ethylene–vinyl acetate copolymers, polystyrene, poly(methyl methacrylate), and polycaprolactone.

On the other hand, there is a wealth of literature[6] concerning iPHB miscible blends with polymers such as poly(vinyl acetate), poly(epichlorohydrin)[7], poly(vinylidene fluoride), poly(ethylene oxide), poly(vinyl alcohol), poly(vinyl phenol) [8,9], cellulose esters, and also synthetic atactic PHB[10]. The incorporation of a second polymer capable of forming miscible blends with iPHB improves,

---

* Corresponding author. Tel.: +34-943-018192; fax: +34-943-212236.
E-mail address: popirsaj@sq.ehu.es (J.J. Iruin).

0032-3861/01/$ - see front matter
PII: S0032-3861(00)00435-3

with more or less success, the physical properties of pure iPHB, as well as leads to a reduction in the price of the final product given the incorporation of a certain percentage of a cheaper component.

However, some of these blends show undesirable side effects. Thus, blending with hydrophilic polymers such as poly(ethylene oxide) or poly(vinyl alcohol), leads to a loss of water resistance with respect to pure iPHB, which is for most applications a desirable property to be retained. In other cases, the biodegradability of the blended system is almost completely lost due to restrictions in the enzymatic access to the iPHB chains [6].

As has been recently pointed out [7], it seems that a prerequisite for the onset of iPHB biodegradation in its miscible blends is that the iPHB chains retain its segmental mobility in the amorphous phase. This condition is achieved when the glass transition (T_g) of the blend remains below the temperature at which the biodegradability is desired, usually room temperature. Thus, the use of low T_g polymers to form miscible blends with iPHB seems particularly desirable. Under this point of view, two polymers among those mentioned above, atactic PHB (aPHB) and poly(epichlorohydrin) (PECH), appear to be promising candidates for blending with bacterial iPHB in order to form useful blends.

The main feature of the iPHB/aPHB system is its 100% biodegradability, in spite of the fact that aPHB does not biodegrade at all when exposed alone to the enzymatic attack [10,11]. It has been stated that the presence of a crystalline phase is a general requirement for the enzymatic hydrolysis of aPHB, a requisite that can be fulfilled by blending with iPHB, among other poly(hydroxyalkanoates) [10,11]. The incorporation of PECH as a second component leads to bioerodible rather than biodegradable blends, where iPHB is the only biodegraded polymer. However, this system still retains a high interest from the applications point of view, particularly if it is considered that, in fact, it is currently the only candidate to form miscible blends with iPHB retaining its characteristics of biodegradability and water resistance, as well as having a large-scale availability and leading to a price reduction with respect to pure iPHB. Furthermore, PECH is considered to show a low permeability to gases and vapours [12,13], which constitutes an additional motivation to choose this elastomer for iPHB modification in the context of the characterisation of its transport properties.

In previous work we have studied the water and carbon dioxide transport in iPHB and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [P(HB-HV)] copolymers [14–16]. Thus, the aim of the present work is to extend this study to the modification of the iPHB transport properties upon the incorporation of aPHB and PECH as miscible low T_g tougheners. Accordingly, this paper will focus on iPHB rich blends, containing up to 40% of aPHB or PECH as second components.

2. Experimental

2.1. Materials

Bacterial iPHB and PECH were obtained from Aldrich. The average molecular weights were $M_n = 262\,000$ and $M_w = 437\,000$ for iPHB, and $M_n = 170\,000$ and $M_w = 976\,000$ for PECH. Atactic iPHB was synthesised by ring opening polymerisation of DL-ß-butyrolactone in toluene solution at 40°C, using a modification of the Et_2Zn/H_2O initiator described in the literature [17]. The catalyst Et_2Zn/H_2O/pyridine (1:0.3:0.12 mol) was used. After 10 days of reaction, the final yield of the isolated dry polymer was 84%. The resulting average molecular weights for aPHB were $M_n = 122\,000$ and $M_w = 233\,000$ (referred to polystyrene calibration standards). The isotactic dyad fraction of the produced polymer was 0.45, as determined by analysis of the ^{13}C NMR spectrum.

2.2. Blend preparation

The semicrystalline iPHB, in powder form, and the rubbery component were premixed in the desired compositions (0, 10, 25, 40 and 75% — only in the iPHB/aPHB case — by weight of the latter) by dissolution in chloroform. After the solvent evaporation, the obtained blend films were stored for two weeks under vacuum for complete removal of the residual traces of solvent. Then, the films were cut into small pieces, and weighted amounts were compression moulded in a Graseby Specac hot press at 195°C for 2 min under a pressure of 2 ton/m^2, after of one minute heating without load. After this process, the mould was transferred to the water-cooling unit attached to the press to allow crystallisation of the isotactic material. Films of 3-cm diameter and constant thickness of approximately 45 and 70 μm were obtained after this procedure. The blend's films were aged under vacuum at room temperature for several months to allow complete crystallisation before the sorption experiments were performed. Additionally, a film of pure PECH was prepared by solvent casting techniques from a chloroform solution, being also stored under vacuum to eliminate the residual solvent.

2.3. Methods

Thermal analysis was performed in a Perkin–Elmer DSC-2C apparatus. Film samples of about 10 mg were first heated from -40 to 200°C at 20°/min, and melting areas and temperatures were determined. From a second scan performed under the same conditions, the glass transition temperatures were measured. The densities of the films were measured at 23°C by means of a density gradient column based on aqueous solutions of sodium bromide. The thickness of the samples was determined with a Duo-Check gauge with an accuracy of 1 μm.

Carbon dioxide sorption experiments were performed in a Cahn D-200 electrobalance enclosed in a thermostated

Table 1
Characterisation of pure polymers and blends

Polymer	T_g (°C)	T_m (°C)	X (%)[a]	X^{iPHB} (%)[a]	Density (g/cm^3)
iPHB	0.6	171.7	62	62	1.237
iPHB/aPHB					
90/10	1.2	172.4	57	63	1.232
75/25	2.2	172.5	48	64	1.227
60/40	3.0	171.3	39	65	1.218
25/75	4.4	168.5	18	73	1.194
0/100	5.3	–	0	0	1.178
iPHB/PECH					
90/10	−1.5	171.2	57	64	1.252
75/25	−4.7	169.6	50	62	1.268
60/40	−7.7	167.4	39	65	1.283
0/100	−23.3	–	0	–	1.360 [20]

[a] Calculated assuming a melting enthalpy value of 132 J/g for the 100% crystalline PHB [19].

cabinet at 30°C [15]. After the polymer samples prepared as stated above were placed in the balance sorption chamber and evacuated overnight, gas at the selected pressure (0.25, 0.5, 0.75 and 1 atm) was admitted in the balance, and the weight change of the sample was recorded. The sorption kinetics obtained in this manner was corrected by subtracting a blank run, obtained under the same conditions of pressure and temperature in each case, but without sample in the balance pan. Corrections for buoyancy effects were also applied.

Water sorption was measured in similar conditions, using a stainless steel container filled with distilled water as the vapour source. Integral sorption experiments were performed in fresh membranes at five different water activities (0.25, 0.5, 0.7, 0.8 and 0.9 approximately), which were selected by changing the set temperature of the water container, as has been described previously [14]. Blank runs were also performed and subtracted from the sorption kinetics. Water permeability was measured at the same temperature by means of a gravimetric permeation cell whose details can be found elsewhere [14,18]. In the upstream side of the membrane water vapour was kept at unity activity for all the experiments, while the activity in the downstream side was 0.35.

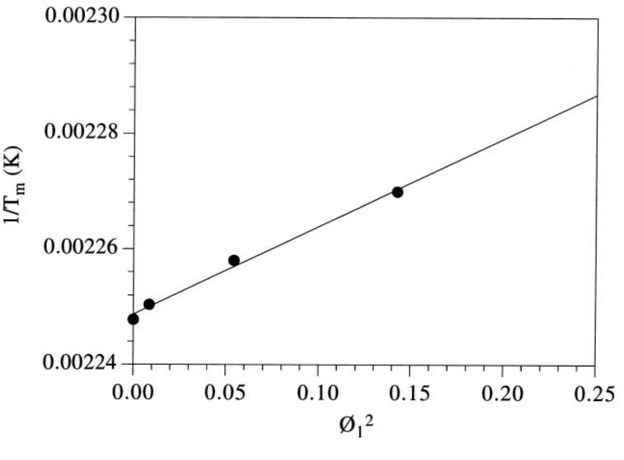


Fig. 1. Reciprocal melting temperature versus square of the amorphous content in iPHB/PECH blends. The solid line represents the best fit of the Nishi–Wang expression (Eq. (1)).

3. Results

3.1. Blend characterisation

The glass transition temperatures (T_g), melting points (T_m) and mass crystallinity degrees (X) obtained from the DSC measurements, together with the densities of the samples, are displayed in Table 1.

Synthetic atactic aPHB and PECH have been shown to form miscible blends with bacterial, semicrystalline iPHB [21,22]. This is confirmed in our samples by the presence of a single T_g between those of the pure polymers, suggesting the existence of a single homogeneous amorphous phase. Another proof of miscibility in blends containing a crystallisable polymer is the depression of the melting temperature upon the incorporation of an amorphous second polymer. Indeed, this is the trend observed for the iPHB/PECH blends in Table 1. However, in the case of iPHB/aPHB, a slight elevation in the melting point was observed for the blends containing 10 and 25% aPHB, then decreasing for the 40 and 75% compositions. Although this behaviour is rather unusual, the occurrence of melting point elevations in miscible polymer blends has already been documented [23,24]. Several hypotheses have been proposed to account for this behaviour, dealing with crystal perfection changes upon blending, crystallite size increase and also crystal perfectioning during the thermal analysis itself. However, there are not many experimental data in the literature on melting point elevations, and the true reasons for this behaviour remain unclear.

The Nishi–Wang treatment provides a relationship between the experimental melting point depression and the degree of interaction between the polymers in the blend, via the interaction parameter [25]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1}\chi\varnothing_1^2 \tag{1}$$

where T_m and T_m^0 are the melting temperatures of the crystallisable polymer in the blend and in the pure state respectively, ΔH_2 is the melting enthalpy of the 100% pure crystalline material per mole of repeating unit, V_1 and V_2 the molar volumes of the repeating units of the amorphous and crystalline polymers, $\varnothing_1$ is the volume fraction of the uncrystallisable component, and χ is the polymer–polymer interaction parameter. Thus, a miscible blend should give a linear behaviour in a 1/T_m versus $\varnothing_1^2$ plot, from which slope the interaction parameter can be determined. This analysis has been applied to the iPHB/PECH blends, using the following values: $V_1 = 68.03\ \mathrm{cm^3/mol}$ [26], $V_2 = 73.14\ \mathrm{cm^3}$ /mol [27] and $\Delta H_2 = 132$ J/g [15,19]. Since our interest here was to assess the state of miscibility of the actual blend samples that will be used in the transport property measurements, Eq. (1) will be applied to the T_m values obtained from the first DSC scan rather than those from the second one. Fig. 1 shows the result of this calculation, giving a value of −0.19 for the interaction parameter. The corresponding interaction energy density (B) takes a value of $-2.5\ \mathrm{cal/cm^3}$, being consistent with different values reported in the literature. For instance, Finelli et al. [7] reported a B-value of $-3.0\ \mathrm{cal/cm^3}$. Dubini Paglia et al. [21] have also studied the same mixture but they have determined equilibrium melting temperatures using Hoffman–Weeks plots. Using their data contained in Table 4 of its paper an average B value of $-3.7\ \mathrm{cal/cm^3}$ can be inferred, although their data seem to be concentration dependent. These results are all consistent with values reported for a series of PECH blends with several aliphatic polyesters [26]. The authors there reported an experimental trend of B as a function of the ratio between aliphatic carbons to ester groups (N). In particular, our value and that of Finelli et al. [7] are close to the value reported [26] for PECH/poly(ethylene adipate) blends. Poly(ethylene adipate) has identical N to that of iPHB. Accordingly, it can be stated that a good miscibility level is achieved between iPHB and PECH after the above blend film preparation procedure.

The crystallinities of the blends investigated are summarised in Table 1. The thermograms of pure aPHB and PECH showed no trace of melting peaks, and their 100% amorphous nature was thus confirmed. Interestingly, the level of crystallinity referred to the isotactic iPHB component (X^{iPHB}) is maintained over the composition range studied, a behaviour that has already been observed [28]. It demonstrates that, in spite of the reduction in the crystallisation kinetics produced upon the addition of the amorphous component, crystallinity develops unimpeded if enough time is allowed for crystallisation. Fig. 2 shows the relationship between the crystallinity and the measured density for the iPHB/aPHB blends. Analytically, this relationship is given by [29]:

$$X(\%) = \frac{d_c}{d}\frac{(d - d_a)}{(d_c - d_a)}100 \qquad (2)$$

where d stands for the experimental blend density, while d_a and d_c are the densities of the amorphous and crystalline phases, respectively, with the assumption that the density of the amorphous iPHB is the same than that of aPHB. This expression can be used to estimate the values of d_a and d_c, by applying a curve fitting procedure to the experimental data. This gives the values $d_a = 1.178\ \mathrm{g/cm^3}$ and $d_c = 1.279\ \mathrm{g/100\ cm^3}$, which are consistent with previously published values (1.179 and 1.279 g/100 cm^3) [29]. This value of the crystalline density is slightly different to the more frequently cited value [27] of 1.260 g/cm^3, which was theoretically calculated from unit cell parameters extracted from X-ray diffraction data. As a criterion, the densities obtained by fitting Eq. (2) to our experimental data will be used thorough this work.

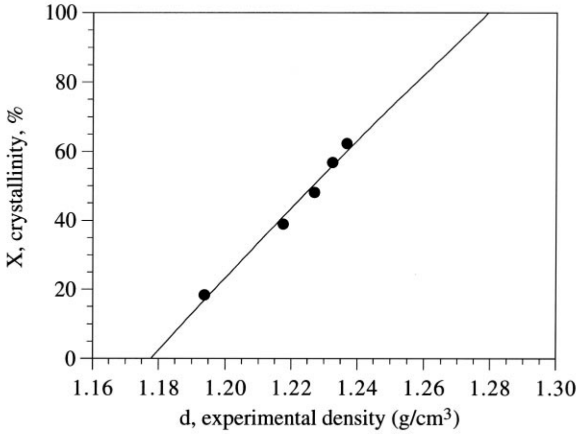


Fig. 2. Crystallinity-density relationships for iPHB/aPHB blends. The solid line represents the best fit of Eq. (2).

3.2. Carbon dioxide sorption measurements

The equilibrium sorption isotherms for CO_2 at 30°C are plotted in Fig. 3a and b for iPHB blends with aPHB and PECH, respectively. The isotherms show a linear behaviour in the pressure range studied, and accordingly may be interpreted in terms of Henry's law, which states the proportionality between the pressure exerted by the penetrant and the gas concentration obtained in the polymer:

$$C = K_H P \qquad (3)$$

where C (cm^3 STP/cm^3) is the gas concentration sorbed in the polymer, K_H (cm^3 STP/cm^3 cm Hg) is the CO_2 solubility coefficient in the polymer and p (cm Hg) is the CO_2 applied pressure. The solubility coefficients, obtained in this manner from the slopes of the concentration against pressure curves, appear in Table 2.

As can be seen in Fig. 3a, the CO_2 sorption increases with the amount of aPHB added to bacterial iPHB. This was an expected behaviour since the effect of aPHB is to decrease the overall crystallinity of the blend in such a manner that more amorphous polymer is available to the CO_2 molecules for sorption, assuming zero gas solubility in the crystalline phase. However, the behaviour of the iPHB/PECH system is less straightforward, given that the blend isotherms appear to overlap with that of iPHB. It is worth noting that, in this case, the situation is complicated due to the superposition of the effects of the blend composition and the crystallinity degree. On the one hand, there is a reduction in the overall degree of crystallinity caused by the dilution effect exerted by the PECH, as was shown in Table 1. However, the PECH present in the amorphous phase has the effect of reducing its carbon dioxide solubility, up to a point that the effect of the crystallinity reduction is compensated by the change in

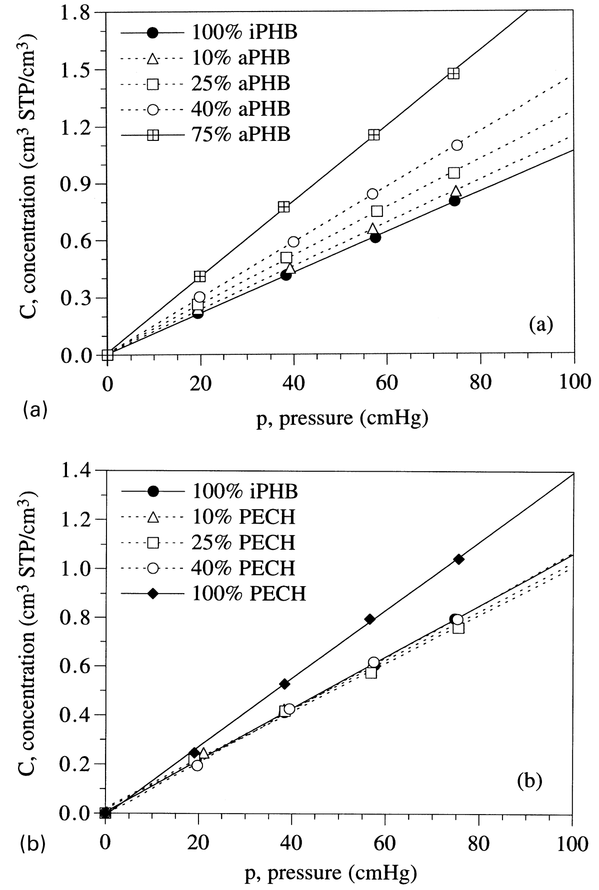


Fig. 3. Carbon dioxide sorption isotherms at 30°C: (a) iPHB/aPHB blends; and (b) iPHB/PECH blends. The weight percent of the second component is indicated in the plots.

solubility due to the blend composition. In fact, if solubilities are recalculated on the basis of the amorphous content of the blends, the iPHB/aPHB isotherms tend to superpose while those of the iPHB/PECH blends spread intermediate to those of the pure components, as is shown in Fig. 4, a behaviour that was masked in Fig. 3b by the effect of crystallinity.

From the Flory–Huggins solution theory for ternary systems in equilibrium, the solubility coefficient in a polymer blend has been shown to be related to the pure components by [12]:

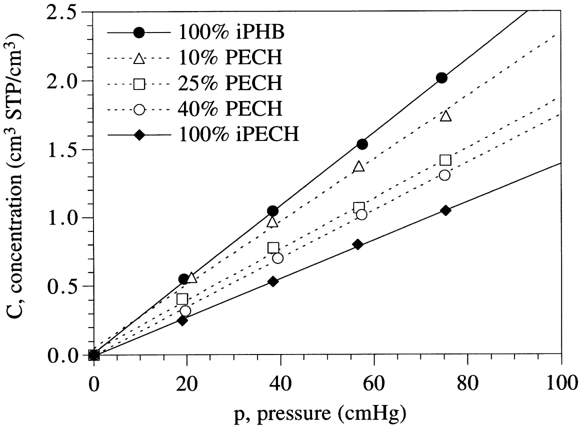


Fig. 4. Carbon dioxide sorption isotherms in iPHB/PECH blends at 30°C, referred to the amorphous polymer.

$$\ln K_H = \varnothing_1 \ln K_{H1} + \varnothing_2 \ln K_{H2} + (BV_3/RT)\varnothing_1\varnothing_2 \qquad (4)$$

where K_H is the Henry's law solubility constant in the miscible blend, K_{H1} and K_{H2} are the corresponding constants for the pure polymers, $\varnothing_1$, $\varnothing_2$ are the volume fractions of the two polymers in the dry blend and V_3 is the molar volume of CO_2 in the condensed state, which has been estimated [30] to be 55 cm^3/mol. Thus, B, the interaction energy density for the polymer pair can be calculated from the sorption measurements. For this purpose, the solubility coefficient has been referred to the amorphous polymer assuming zero sorption in the crystalline phase. Accordingly, the volume fractions $\varnothing_1$ and $\varnothing_2$ have been calculated on an amorphous basis, assuming that the PECH chains are rejected into the amorphous phase during the iPHB spherulite growth period, so that the polymeric system may be considered as a mixture of pure iPHB crystals and a homogeneous miscible blend of uncrystallized iPHB and PECH molecules [21,22].

The results of such calculations are shown in Fig. 5, where the solid line is the best fit of Eq. (4) (with K_H^{am} and $\varnothing_{PECH}^{am}$ instead of K_H and $\varnothing_2$). This fit gives a value for the interaction energy density of -0.60 cal/cm^3 at 30°C. The result is certainly different to those reported in papers concerning melting point depression. However, different

Table 2
Sorption and diffusion coefficients for carbon dioxide in iPHB blends

% aPHB or % PECH	iPHB/aPHB Blends		iPHB/PECH Blends	
	K_H (cm^3STP/cm^3 cm Hg)	D (10^{-9} cm^2/s)	K_H (cm^3 STP/cm^3 cm Hg)	D (10^{-9} cm^2/s)
0	0.0106	4.43	0.0106	4.43
10	0.0114	4.67	0.0101	5.30
25	0.0127	5.80	0.0100	7.25
40	0.0146	6.58	0.0107	8.52
75	0.0198	24.9	–	–

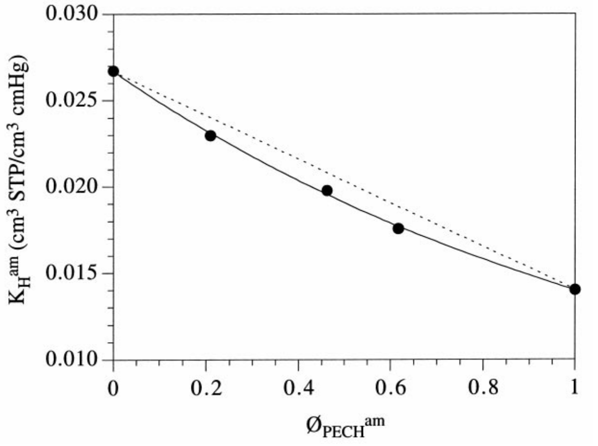


Fig. 5. Best fitting of the Flory–Huggins equation for ternary systems after Eq. (4).

reasons can be argued in order to explain such a kind of discrepancy. As Sanchez [31] pointed out some years ago, if the interaction parameter or *B* is concentration dependent, it is possible to define different *B* parameters depending on the type of experimental measurements used. The reason is that every one of these techniques extracts *B*-values from different chemical potentials of the blend components or from the chemical potential of the probe used to investigate the mixture, as is the case of carbon dioxide in our sorption measurements. As we have previously mentioned, Dubini Paglia et al. [21] data seem to confirm a concentration dependence of the *B* parameter. On the other hand, strong temperature dependence of the *B* parameter [32] can be possible, depending on the location of the upper and lower critical solution temperatures of the blend. So, the discrepancy between this value and the obtained from the melting point depression treatment at temperatures around 170°C was not totally unexpected.

Gases at low pressures, or, in a more general sense, penetrants at low activities when swelling stresses are negligible and relaxation is accordingly immeasurable, usually diffuse into polymer materials according to the well-known Fick's laws (also called Case I diffusion) [33], with constant diffusion coefficients. Thus, from the transient part of the sorption rate curves, prior to equilibrium sorption was reached, CO_2 diffusion coefficients in iPHB and its blends were calculated using the long-term solution of Fick's diffusion equation [34]. Some representative results are shown in Fig. 6 as a function of the applied pressure.

Although the data show some scatter, it seems reasonable to accept that diffusivity is essentially concentration independent in the investigated pressure range [15]. The diffusion coefficients obtained as the average of the individual values such as those appearing in Fig. 6 are displayed in Table 2. The linearity of the sorption isotherms, together with the constancy of the diffusion coefficients, constitutes the usual behaviour in rubbery polymers at moderate pressures, when plasticization of the polymer by the penetrant may well be considered negligible. As can be seen in Table 2, the apparent CO_2 solubility in the iPHB/aPHB blends is clearly higher than in iPHB blends with PECH. By the contrary, the behaviour of the diffusion coefficients is the opposite, being higher for the iPHB/PECH system. This is consistent with the lower T_g and the related higher mobility of the amorphous phase in the iPHB/PECH blends, leading to a facilitated transport of the CO_2 molecules through the polymeric media. Given that both the solubility and diffusion coefficients are essentially constant, as has already been shown, the permeability (*P*) can be calculated from the product of these coefficients after [33,34]:

$$P = 10^{10} K_H D \tag{5}$$

being *P* expressed in barrers (1 Barrer = 10^{-10} cm³ cm/cm² s cm Hg). The result is plotted in Fig. 7. Interestingly, the trends made evident by the solubility and diffusion coefficients tend to compensate in such a manner that both systems, iPHB/aPHB and iPHB/PECH, show virtually the same permeability to carbon dioxide at each composition.

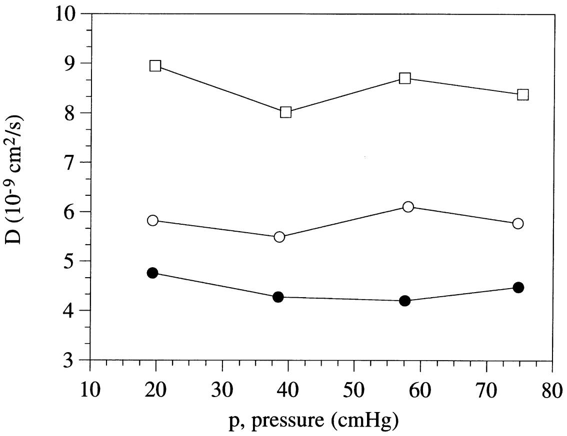


Fig. 6. Some representative carbon dioxide diffusion coefficients in iPHB and two blends at 30°C: ●, iPHB; ○, iPHB/25% aPHB; □, iPHB/40% PECH.

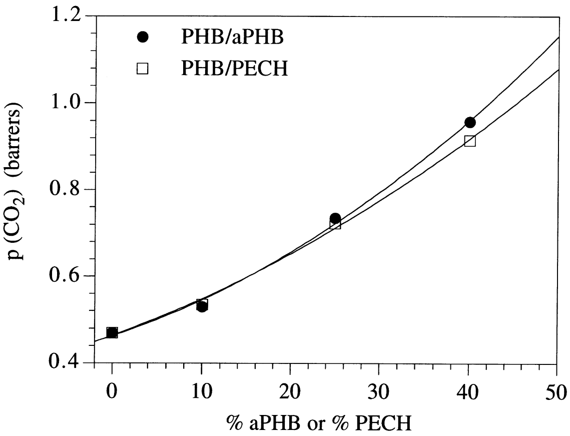


Fig. 7. Carbon dioxide permeability through iPHB/aPHB and iPHB/PECH blends at 30°C.

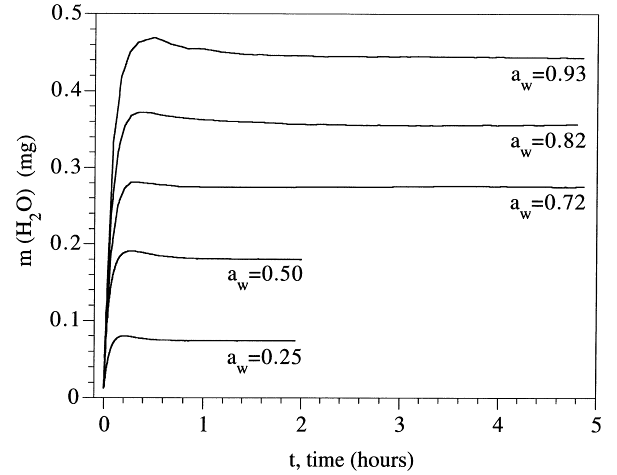


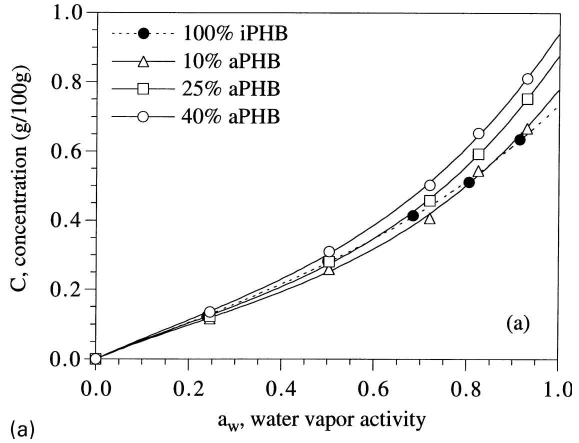
Fig. 8. Water sorption kinetics in an iPHB/40% aPHB blend film at 30°C.

3.3. Water vapour sorption and permeation measurements

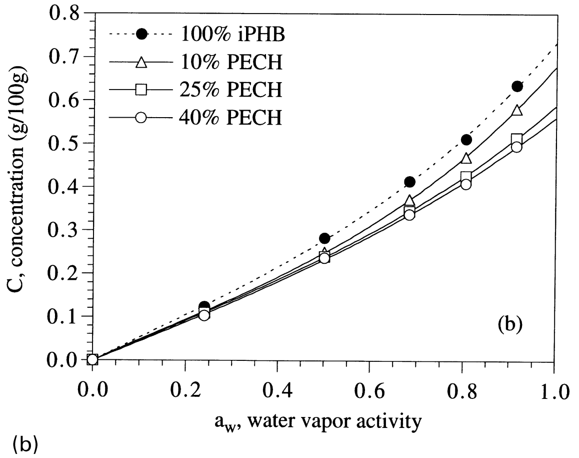
Water sorption in iPHB-based blends was investigated at 30°C in 75 μm films. The water sorption process is characterised by the existence of a small peak in the water take-up versus time plots. Under the experimental conditions applied in this work, the difference between the peak water sorption and the equilibrium sorption is always in the 2–4% range, with no pattern in the dependence of this percentage on the water activity or the blend composition. To illustrate this behaviour, a complete set of water sorption kinetics corresponding to the iPHB/40%aPHB blend is shown in Fig. 8 for reference, illustrating the shape of the sorption curves and the time scale involved. It is interesting to note that, as sorption experiments previously performed have shown [14], the weight loss after the maximum can be as high as a 30% at 40°C and high activities for iPHB solvent cast samples, up to three days being necessary to reach equilibrium. However, the equilibrium sorption levels were consistent with those recorded in this work for melt pressed iPHB samples.

The resulting equilibrium sorption isotherms are displayed in Fig. 9. As can be seen in this figure, the addition of aPHB leads to a general increment in the sorption levels that can be attributed to the decrease in the overall crystallinity. On the contrary, the water solubility decreases with the amount of PECH in the blend, in spite of the reduction in the crystallinity. These trends are consistent with the previously reported dependence of the CO_2 sorption isotherms on the blend composition.

In spite of the shape of the sorption kinetics, application of the Fick's long-term diffusion equation to the initial transient part of the curves gave straight lines, indicating that the entrance of the water molecules into the initially penetrant free polymer proceeds according to the Fickian (or Case I) model, as reported previously [14]. The diffusion coefficients calculated in this way are displayed in Fig. 10. The dependence of diffusivity on the equilibrium concentration is essentially linear (except for the blends containing 25 and 40% PECH), so that a diffusion coefficient corresponding to a zero concentration of penetrant can be easily extrapolated. In general terms, the diffusion coefficient for the iPHB/aPHB blends tend to be slightly higher than those for the iPHB/PECH system, as opposed to the observed behaviour for carbon dioxide.



(a)



(b)

Fig. 9. Water sorption isotherms at 30°C: (a) iPHB/aPHB blends; and (b) iPHB/PECH blends.

The upward curvature of the sorption isotherms, together with the decrease of the diffusion coefficients with activity is usually interpreted as an indication of the existence of the clustering phenomenon [34,35]. It means that there is a tendency for the sorbed water molecules to associate or form clusters due to the pre-eminence of water–water over water–polymer interactions. The classical analysis of Zimm and Lundberg [36] provides a means for quantifying the extent of clustering from the sorption data. Thus, by applying the following equation:

$$\frac{G_{ww}}{V_w} = -(1 - \varnothing_w)\left[\frac{\partial(a_w/\varnothing_w)}{\partial a_w}\right]_{P,T} - 1 \tag{6}$$

the clustering function (G_{ww}/V_w) can be evaluated. Here V_w is the water molecular volume; $\varnothing_w$, the water volume

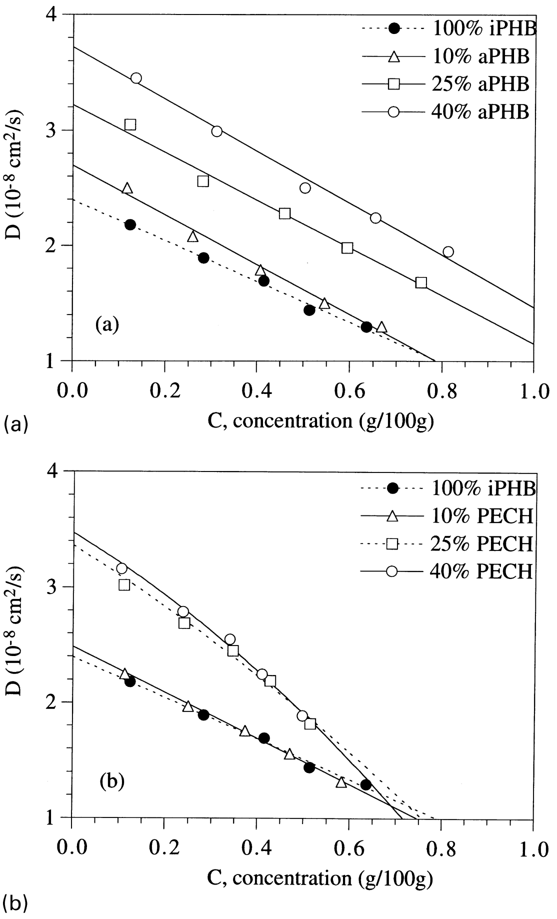


Fig. 10. Water diffusion coefficients at 30°C: (a) iPHB/aPHB blends; and (b) iPHB/PECH blends.

fraction referred to the amorphous polymer; and a_{w} is the water vapour activity. In this manner, the average number of water molecules, which exist in a cluster, or the cluster size, can be easily estimated as the quantity $(1 + \varnothing_{\mathrm{w}} G_{\mathrm{w}} / V_{\mathrm{w}})$. Application of this treatment to our experimental data indicates a low, but significant tendency to cluster formation for all blends at water activities of 0.5 and above (see Fig. 11). Cluster formation is favoured in iPHB/aPHB blends with respect to pure iPHB, while the effect of PECH is to reduce the average cluster size.

Water vapour transmission rates (WVTR) were experimentally measured for iPHB and its blends at 30°C by triplicate to ensure reproducibility. The results obtained are plotted in Fig. 12 as a function of the blend composition. As was expected, atactic iPHB has the effect of increasing the permeability; PECH also increases the WVTR of the blends with respect to iPHB, although this increment remains essentially constant with the blend composition in the range investigated. Again, this behaviour may be interpreted as a result of the compromise between the reduction in the degree of crystallinity and the lowering in the permeability of the amorphous phase exerted by the poly(epichlorohydrin).

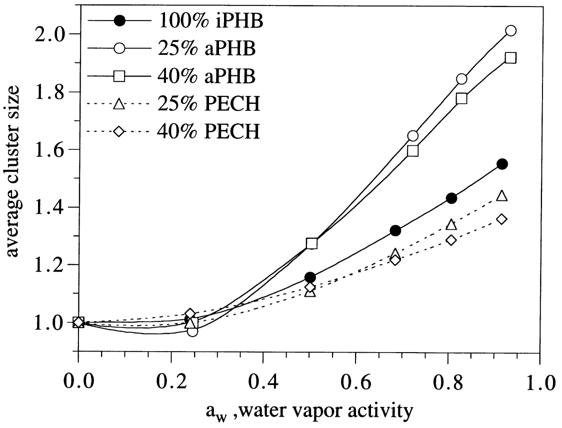


Fig. 11. Average water cluster sizes in iPHB and some of its blends at 30°C.

3.4. iPHB/aPHB blends: influence of crystallinity

In semicrystalline polymers, the crystalline regions are generally considered impenetrable to penetrants, with few exceptions [37]. This has led to the general observation that semicrystalline polymers tend to exhibit better barrier properties than amorphous polymers. In the most widely accepted view of the diffusion process in semicrystalline polymers, the diffusivity is considered to be reduced with respect to the completely amorphous polymer by a "geometric impedance factor" (τ), related to the more tortuous path that the penetrant molecules must follow in order to bypass the impermeable crystals, and a "chain immobilisation factor" (β), accounting for the crosslinking effect of the crystallites of the amorphous chains that restricts their mobility [38]. From this model, the effective diffusivity can be expressed as:

$$D = \frac{D^{\mathrm{am}}}{\tau\beta} \tag{7}$$

where D^{am} stands for the diffusivity in the amorphous polymer. However, a good deal of experimental data can be

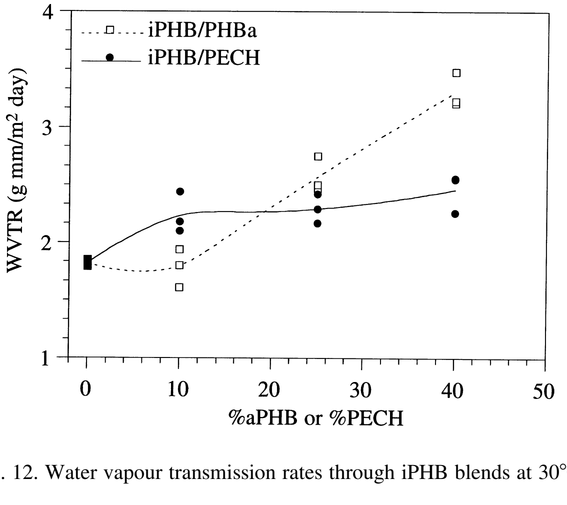


Fig. 12. Water vapour transmission rates through iPHB blends at 30°C.

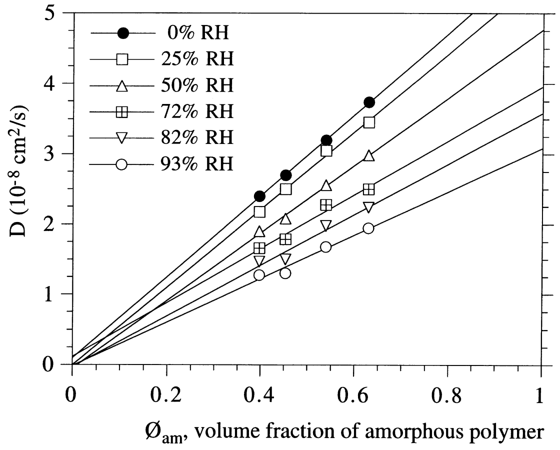


Fig. 13. Water diffusion coefficients in iPHB/aPHB blends as a function of the volume fraction of amorphous polymer in the sample at 30°C.

Table 3
Amorphous diffusion coefficients for water vapour in iPHB/aPHB blends

Water activity	D^{am} (10^{-8} cm^2/s)
0.000	5.97[a]
0.246	5.54
0.504	4.72
0.720	4.08
0.825	3.56
0.930	3.08

[a] Calculated using extrapolated values.

adequately described [39] by approximating the product $(\tau\beta)^{-1}$ by the amorphous phase volume fraction, so that the later equation gives

$$D = D^{am}\varnothing_{am} \tag{8}$$

where $\varnothing_{am}$ is the volume fraction of amorphous phase, which is given in Ref. [12]:

$$\varnothing_{am} = 1 - (d/d_c)X \tag{9}$$

This expression was successfully applied in the past to interpret the water diffusion coefficients in PET, polyamide(6,10) and polyethylene [40]. In Fig. 13 the water diffusion coefficients for the iPHB/aPHB blends are plotted as a function of the volume fraction of amorphous polymer at different activities. From this figure, it is clear that the water diffusion coefficients increase linearly with the amorphous content of the polymer, indicating that Eq. (8) is able

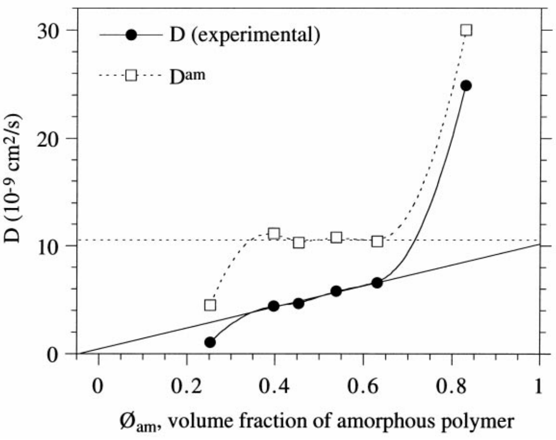


Fig. 14. CO_2 diffusion coefficients in iPHB/aPHB blends at 30°C. Closed symbols: experimental results; open symbols: calculated amorphous diffusion coefficients (see text for details).

to describe the water/iPHB system, at least in the crystallinity range here investigated. Accordingly, from the slopes of the lines shown in Fig. 13, the amorphous diffusion coefficient can be obtained for each value of the water activity. These are summarised in Table 3. Since they have not been determined experimentally, it cannot be assured that these values actually correspond to the true diffusion coefficients in the 100% amorphous polymer. However, this treatment shows that the water diffusivity in iPHB can be predicted after a combination of Eq. (8) and Table 3 for a range of intermediate crystallinities.

This analysis can also be extended to carbon dioxide diffusion. In this case, data for a range of iPHB/(0–75%)aPHB blends covering a crystallinity interval of 18–68% are available, as well a previously reported [15] CO_2 diffusion coefficient of 1.1×10^{-9} cm^2/s in a iPHB sample of 77% crystallinity. All these values are plotted against the volume fraction of amorphous polymer in Fig. 14 (closed symbols). As can be observed, the diffusion coefficients corresponding to the samples of intermediate crystallinities fall in a straight line passing through the origin, as in the case of water diffusivities. However, the diffusion data for the two samples with the lowest and highest crystallinities deviate from this trend, thus indicating the limitations of this simplistic model. This situation is made even more evident if the amorphous diffusion coefficients, calculated individually for each data point as $D^{am} = D/\varnothing_{am}$, are plotted in a similar fashion (see Fig. 14, open symbols).

Summing up, the above analysis has shown the usefulness

Table 4
Comparative of transport and mechanical properties [10] for iPHB and iPHB/25%aPHB

Polymer	CO_2 Permeability (barrers)	WVTR (g mm/m^2 day)	Young's modulus [10] (Mpa)	Tensile strength [10] (MPa)	Elongation at break 10 (%)
iPHB	0.47	1.82	1560	38	5
iPHB/APHB 75/25	0.74	2.57	260	20	210

of the model represented by Eq. (8) for the description of the diffusion features of water and carbon dioxide in iPHB, a pair of penetrants of quite different nature, making also evident its limited predicting ability outside the intermediate range of crystallinities.

4. Summary and conclusions

The solubility, diffusivity and permeability of carbon dioxide and water vapour are reported for iPHB blends containing up to 40% synthetic atactic aPHB or poly(epichlorohydrin). iPHB/aPHB blends showed a higher solubility of water and CO_2 than iPHB/PECH, having also higher water vapour transmission rates in general terms. Interestingly, CO_2 solubility and water permeability was essentially the same for the three iPHB/PECH blends investigated, which may be interpreted as a consequence of the combined effect of crystallinity and blend composition. Another remarkable observation was that carbon dioxide permeability is the same for both blends at each composition, in spite of the opposing trends shown by the respective solubility and diffusion coefficients.

Finally, it is worth comparing the effect of blending on the iPHB transport properties, with the change in its mechanical properties, as reported in the literature [10]. As can be seen in Table 4, the incorporation of a 25% aPHB has the effect of increasing the flexibility and elongation to break of pure bacterial iPHB by a factor of 6 and 40, respectively, while the CO_2 and water permeability are only about 1.5 times higher. These observations indicate that, blending iPHB with rubbery polymers such as aPHB and PECH, can be good way to obtain new materials with improved mechanical properties with a somewhat limited loss of its originally good barrier character.

Acknowledgements

Financial support of UPV (project no. 203.215-EB173/95) and CICYT (project n. MAT98/0530) is gratefully acknowledged. We also thank the Departamento de Economía de la Diputación de Gipuzkoa for the financial support received. O.M. thanks the Basque Government for a PhD grant.

References

[1] Holmes PA. Phys Technol 1985;16:35.
[2] Pouton CW, Akhtar S. Adv Drug Deliv Rev 1996;18:136.
[3] Byrom D. Int Biodet Biodegrad 1993;31:199.
[4] Inoue Y, Yoshie N. Prog Polym Sci 1992;15:571.
[5] Doi Y. Macromol Symp 1995;98:585.
[6] Verhoogt H, Ramsay BA, Favis BD. Polymer 1994;35:5155.
[7] Finelli L, Sarti B, Scandola M. J Mater Sci Pure Appl Chem 1997;A34:13.
[8] Iriondo PJ, Iruin JJ, Fernandez-Berridi MJ. Polymer 1995;36:3235.
[9] Iriondo PJ, Iruin JJ, Fernandez-Berridi MJ. Macromolecules 1996;17:5605.
[10] Abe H, Matsubara I, Doi Y. Macromolecules 1995;28:844.
[11] Scandola M, Focarete ML, Adamus G, Sikorska W, Baranowska I, Swierczek S, Gnatowski W, Kowalczuk M, Jedlinski Z. Macromolecules 1997;30:2568.
[12] Chiou JS, Barlow JW, Paul DR. J Appl Polym Sci 1985;30:1173.
[13] Body RW, Kyllingstad VL. In: Mark HF, Bikales NM, Overberger CG, Menges G, editors. Encyclopedia of polymer science and engineering, vol. 6. New York: Wiley, 1986. p. 308–15.
[14] Miguel O, Iruin JJ. J Appl Polym Sci 1999;73:455.
[15] Miguel O, Barbari TA, Iruin JJ. J Appl Polym Sci 1999;71:2391.
[16] Miguel O, Iruin JJ. Macromol Symp 1999;144:427.
[17] Agostini DE, Lando JB, Reid Shelton J. J Polym Sci Part A 1971;9:2775.
[18] Miguel O, Fernandez-Berridi MJ, Iruin JJ. J Appl Polym Sci 1997;64:1849.
[19] Sanchez Cuesta M, Martinez Salazar J, Barker PA, Barham PJ. J Mater Sci 1992;27:5335.
[20] Aldrich product information.
[21] Dubini Paglia E, Beltrame PL, Canetti M, Seves A, Marcandalli B, Martuscelli E. Polymer 1993;34:996.
[22] Sadocco P, Canetti M, Seves A, Martuscelli E. Polymer 1993;34:3668.
[23] Runt J, Rim PB, Howe SE. Polym Bull 1984;11:517.
[24] Rim PB, Runt J. Macromolecules 1983;16:762.
[25] Nishi T, Wang TT. Macromolecules 1975;8:909.
[26] Fernandes AC, Barlow JW, Paul DR. J Appl Polym Sci 1984;29:1971.
[27] Barham PJ, Keller A, Otum EL, Holmes PA. J Mater Sci 1984;19:2781.
[28] Pearce R, Marchessault RH. Polymer 1994;35:3990.
[29] de Koning GJM, Scheeren AHC, Lemstra PJ, Peeters M, Reynaers H. Polymer 1994;35:4598.
[30] Toi K, Paul DR. Macromolecules 1982;15:1104.
[31] Sanchez IC. Polymer 1989;30:471.
[32] Etxeberria A, Iriarte M, Uriarte C, Iruin JJ. Macromolecules 1995;28:7188.
[33] Felder RM, Huvard GS. Methods of experimental physics, vol. 16c. New York: Academic Press, 1980 (p. 334–8).
[34] Vieth WR. Diffusion in and through polymers. Munchen: Hanser, 1991.
[35] Schult KA, Paul DR. J Polym Sci, Polym Phys Ed 1996;37:2805.
[36] Zimm BH, Lundberg JL. J Phys Chem 1956;60:425.
[37] Hedenqvist M, Gedde UW. Prog Polym Sci 1996;21:299.
[38] Michaels AS, Bixler HJ. J Polym Sci 1961;50:393.
[39] Paul DR. Ber Bunsen-Ges Phys Chem 1979;83:294.
[40] Lasoski SW, Cobbs WH. J Polym Sci 1959;36:21.