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Blends of bacterial poly(3-hydroxybutyrate) and a poly(epichlorohydrin-*co*-ethylene oxide) copolymer: thermal and CO_2 transport properties

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Abstract

In this work the miscibility and the carbon dioxide transport properties of a bacterial, isotactic poly(3-hydroxybutyrate) (iPHB) and its blends with a copolymer of epichlorohydrin and ethylene oxide (ECH-*co*-EO) have been studied. Blends were prepared by solution/precipitation. The aim to obtain miscible blends of iPHB with a rubbery second component (such as the ECH-*co*-EO copolymer) is to have mixtures with glass transition temperatures below room temperature. In these conditions, the iPHB chains not involved in the crystalline regions retain its mobility. This mobility seems to be necessary for the attack of microorganisms and the corresponding biodegradability.

Miscibility is the general rule of these mixtures, as shown by the existence of a single glass transition temperature for each blend and by the depression of the iPHB melting point. The interaction energy density stabilising the mixtures, calculated using the Nishi–Wang treatment, was similar to those of other polymer mixtures involving different polyesters and poly(epichlorohydrin) (PECH) and ECH-*co*-EO copolymers. The so-called binary interaction model has been used in order to simulate the evolution of the interaction energy density with the ECH-*co*-EO copolymer composition. Previously reported experimental data on blends of iPHB with PECH and poly(ethylene oxide) (PEO) have been used to quantify the required segmental interaction energy densities.

In the determination of the CO_2 transport properties of the mixtures, only iPHB rich blends containing up to 40% of copolymer were considered. The effect of the ECH-*co*-EO copolymer is to increase the sorption and the diffusion of the penetrant (and, consequently, the permeability) with respect to the values of the pure iPHB. This is primarily due to the reduction of the global crystallinity of the blends and to the low barrier character of the ECH-*co*-EO copolymer. Sorption data can be reasonably reproduced using an extension of the Henry's law to ternary systems.

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

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1. Introduction

The most studied and easily produced member of the biodegradable family of polymers denoted as poly(hydroxyalkanoate)s is poly(3-hydroxybutyrate), (iPHB), an isotactic high molecular weight polymer with a melting point around 430–450 K, and a glass transition temperature close to 278 K. iPHB is a naturally occurring, thermoplastic polyester, produced in the form of intracellular granules by several microorganisms as carbon and energy storage material. It is a truly biodegradable and excellent biocompatible material, suitable for two promising applications. One is as a viable candidate for packaging applications relieving the environmental concern caused by the disposal of other non-biodegradable plastics. The other potential application is to provide new-type of biomedical products for drug release and sutures. In both cases, the transport properties of gases and vapours (water) through the material have to be taken into account.

However, its prohibitive cost, the narrow difference between the temperatures of thermal degradation and processability and the high crystalline content, which gives rise to poor mechanical properties [1], have prevented an extended use of iPHB in the packaging industry. Different alternatives have been proposed in order to

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improve iPHB properties. For instance, literature contains examples of the preparation of blends with other synthetic polymers [2–10], the copolymerisation with a second monomer [11] or the use of mixtures with other copolymers [12]. One of the best known alternatives, maintaining the biodegradability of the final product, is the biosynthesis of copolyesters containing 3-hydroxyalkanoate units other than 3-hydroxybutyrate, using a variety of bacteria. Among the comonomers, 3-hydroxyvalerate, 4-hydroxybutyrate or 3-hydroxyhexanoate are commonly cited [13]. The final copolyesters are intended to show an increased toughness by incorporating more flexible units in the polymeric chain, as well as a decrease in the melting point, minimising the risk of thermal degradation during processing.

Alternatively, iPHB has been modified preparing mixtures with oligomeric second components. Biodegradable low molecular weight additives, such as citrates, dodecanol, lauric acid or tributyrin, have been reported [14].

As far as the iPHB blends is concerned, it has been reported [15] that miscible blends in which the mixture is in the glassy state do not maintain the iPHB biodegradability, due to the restrictions caused in the segmental mobility of the amorphous phase. The opposite effect is observed when the glass transition of the blend remains below the room temperature at which biodegradability occurs. Thus, the use of low T_g polymers to form miscible blends with iPHB seems particularly desirable. It should be pointed out that the amorphous regions of pure iPHB are rubbery at room temperature.

In this context, miscible blends of iPHB and rubbery poly(epichlorohydrin) (PECH) have received a particular attention in the last years [6,14–16]. Finelli et al. [15] have reported a blend of iPHB with 20% of PECH that biodegrades both in enzymatic solution and in activate sludge. Comparing these data with those of miscible iPHB/Cellulose acetate butyrate blends that did not biodegrade, the main conclusion was that differences could be attributed to the different mobility of the interlamellar mixed phase. In the blend with PECH, iPHB chains in the amorphous phase are in the rubbery state, whereas in the other blend their mobility is hindered by its T_g above room temperature. Using the same idea, miscible mixtures of bacterial, isotactic PHB (iPHB) with synthetic, atactic and completely rubbery PHB (aPHB) have been prepared and characterized [14,17,18].

Different authors have reported miscible blends of iPHB and other halogenated polymers [19]. In all cases, miscibility has been attributed to specific interactions between the carbonyl group of the polyesters and the chlorine moiety of the halogenated second components.

Rubbery copolymers of epichlorohydrin and ethylene oxide (ECH-*co*-EO) are good candidates for blending with bacterial iPHB in order to get useful blends. iPHB is miscible with PEO [10] and PECH [15] and the incorporation of their copolymers to iPHB could improve physical properties such as fragility or thermal stability. The copolymers have also low T_g values, allowing the iPHB amorphous regions to retain the mobility and the progression of the biodegradation process. Recently, data concerning the crystallization and melting behaviour of two bacterial polyesters blended with a copolymer of epichlorohydrin and ethylene oxide have been reported [20].

In this paper, after testing the miscibility of iPHB and a (ECH-*co*-EO) copolymer, we have investigated the transport properties of these blends as potential candidates in the packaging industry. PEO based films show interesting properties in terms of CO_2 permselectivity. Given that membranes based on PEO show problems to form free stand films, there have been many attempts to copolymerise EO with different comonomers [21–24]. Recently, copolymers of ethylene oxide with epichlorohydrin of different composition have been investigated [25] in order to determine their transport properties.

This paper is an extension of our previous work on the transport properties of gases and vapours through iPHB/-PECH blends [26]. The miscibility has been studied by thermal analysis (DSC), following the evolution of the glass transition of the blends with the composition. The interactions stabilising the mixtures have been quantified through the Flory–Huggins interaction parameter and the related interaction energy density. Both were calculated from the melting point depression of the iPHB crystals as a consequence of the presence of the (ECH-*co*-EO) amorphous copolymer in the blends. Transport properties have been determined using gravimetric sorption experiments.

2. Experimental section

2.1. Materials

iPHB was obtained from Biomer, Germany. Its average molecular masses, determined by SEC-GPC at 303 K in chloroform were $\bar{M}_w = 374,000$ g/mol and $\bar{M}_n = 220,000$ g/mol. However, these SEC results must be taken with caution, giving the limited solubility of the polymer in chloroform (see below).

A copolymer of epichlorohydrin and ethylene oxide was supplied by Scientific Polymer Products. The ECH content was 70% by weight, as determined by ^{13}C NMR (Varian 200 spectrometer) in DMSO. It is a rubbery material with a glass transition temperature at 234 K. The weight and number average molecular masses (determined by GPC in THF and 303 K as PS samples) were 725,000 and 410,000 g/mol, respectively.

2.2. Blend preparation

It is pertinent to comment the problems found in preparing the blends. In previous papers of this group [26, 27] different blends of iPHB (obtained from Aldrich) were prepared both by casting from chloroform solutions and by solution/precipitation in chloroform/*n*-hexane mixture. However, it was impossible to dissolve the iPHB from Biomer in chloroform in the adequate concentrations for casting. This seems to indicate the existence of some differences between the characteristics of both bacterial samples. Some additional comments about this problem will be detailed in the next section.

In order to prepare the mixtures it was then necessary to resort to an unusual solvent such as epichlorohydrin. Although clear, homogeneous solutions were relatively easy to obtain, cast films from these solutions were difficult to dry completely. So, blends were finally obtained by a solution/precipitation method using epichlorohydrin as solvent and cold hexane as precipitant.

In order to obtain appropriate films, the isotactic PHB, (iPHB), and the copolymer were premixed in the desired compositions by the method above mentioned (epichlorhydrin to reflux/cold hexane). They were repeatedly washed with hexane in order to eliminate epichlorohydrin. After being kept under a UV lamp for 24 h, the premixed samples were stored for four days under vacuum and 373 K in order to remove the precipitant. The process was followed by a compression moulding in a Graseby Specac hot press at 458 K for 2 min under a pressure of 2 t/m^2. After this process, the mould was transferred to the cooling system attached to the press in order to allow iPHB crystallisation. The blend films were stored for other 4 days under vacuum and 373 K for removal of the residual traces of precipitant. Finally, they were stored under vacuum and room temperature until thermal or sorption experiments were performed.

2.3. Methods

Thermal analysis was performed in a Perkin–Elmer DSC-2C apparatus, with a TADS Data Station. Melting point temperatures were determined during a first scan from 250 to 473 K at 20 K/min. After 1 min at 473 K in order to eliminate the previous thermal history, samples were quenched down to 250 K at the maximum nominal cooling rate (320 K/min) of the calorimeter. A second scan, in identical conditions to the first one, was performed in order to determine the glass transition temperature of the samples.

The density of the films used in sorption experiments was determined at 296 K in a density gradient column using aqueous solutions of NaBr. The estimated accuracy was 0.0007 g/cm^3. The thickness was measured by a Duo Check gauge, with an accuracy of 1 μm. The required crystallinities were determined from the DSC experiments above described.

Carbon dioxide sorption experiments were performed in a Cahn D-200 electrobalance enclosed in a thermostated box at 303 K. After hanging up the polymer films, the balance sorption chamber was evacuated overnight. Carbon dioxide was then admitted in the balance at different pressures up to the atmospheric one, and the weight change of the sample was recorded. Sorption data were corrected by taking into account buoyancy effects and by subtracting a blank run, obtained under the same conditions but without sample.

3. Results and discussion

3.1. iPHB characterization

As previously mentioned, the iPHB sample used in this paper (from Biomer, Germany) is partially insoluble in chloroform whereas, the iPHB from Aldrich (which has been used in previous papers of this and other groups) forms homogeneous solutions in this solvent. This is not the only difference between these two commercial polymers. Whereas, the first one has a melting point of 451 K and a 67% of crystallinity (DSC), the second one usually exhibits melting points around 433 K and a 61% of crystallinity (DSC). In order to know more about the origin of such differences, a ^{13}C NMR study of both polymers in a mixture of chloroform and trifluoroacetic acid was undertaken. We hypothesized that such different properties could arise from differences in the stereoregular microstructure (tacticity) of the two samples.

We have used the stereoregular sensibility of the methylene unit carbon in order to quantify this tacticity. This carbon signal exhibits two peaks at 41.1 (*m* diad) and 40.9 (*r* diad). The quantitative analysis showed small differences (if any) between the two samples. The Biomer sample was 99.2% isotactic whereas the Aldrich one was 99.0%. These differences cannot be in the origin of the differences in melting points and crystallinity of the two samples. For instance, literature data [28] have previously shown that it is necessary to go down to an 85% of isotacticity in order to decrease melting points in 9°. Other possibilities such as the influence of some nucleating agents, the percentage of R- and L- stereoisomers, etc. must be considered before extracting some conclusions about the different behaviour of these two samples.

3.2. Thermal properties of the blends. Determination of the interaction energy density

A single, composition dependent, glass transition temperature was obtained in all investigated samples (see Fig. 1), a macroscopic evidence of blend miscibility. The appearance of a sigmoid T_g-composition behaviour in miscible blends has been attributed to the existence of specific interactions between the polymer components [29].

The blend miscibility was corroborated after measuring the melting points of the different blends where iPHB crystallizes. The data are reported in Table 1, showing a continuous melting point depression of the iPHB crystals when the concentration of the copolymer increases.

These data can be used in order to quantify the

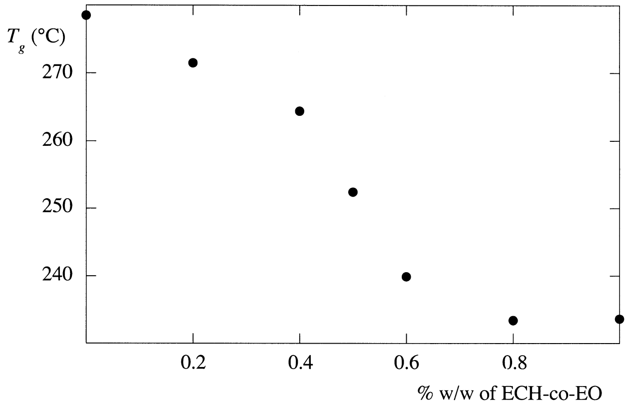

Fig. 1. Glass transition temperatures of blends of iPHB and the ECH-*co*-EO copolymer, covering the whole range of compositions.

interactions that are responsible of the observed miscibility. We have followed the Nishi–Wang treatment [30], from which the so-called Flory–Huggins interaction parameter (χ_{12}) can be calculated using the equation:

$$\left(\frac{1}{T_\mathrm{M}}\right)-\left(\frac{1}{T_\mathrm{M}^0}\right)=\left(\frac{-RV_2}{\Delta H_2 V_1}\right)\chi_{12}\phi_1^2 \tag{1}$$

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 enthalpy of fusion of the 100% pure crystalline material per mole of repeating units, V_1 and V_2 are the molar volumes of the repeating units of the amorphous and the semicrystalline polymers and ϕ_1 is the volume fraction of the uncrystallisable component. According to Eq. (1), a miscible blend should give a linear $1/T_\mathrm{M}$ vs. ϕ_1^2 plot. From the slope the interaction parameter χ_{12} can be determined. Fig. 2 shows a Nishi–Wang plot for our blends. From this plot an interaction parameter value of -0.13 was obtained, when the following values were used: $V_2 = 68.03\ \mathrm{cm^3/mol}$ [31], $V_1 = 53.79\ \mathrm{cm^3/mol}$ [20] and $\Delta H_2 = 132\ \mathrm{J/g}$ [32].

It is more convenient to express the interaction level by using the so-called interaction energy density B, which expresses the interaction energy per volume unit. This B is related to χ_{12} by means of the next equation:

$$B=\frac{RT\chi_{12}}{V_1} \tag{2}$$

where the molar volume of amorphous component is used as a reference. With this change we eliminate the problem of the segmental reference volume implicit in the definition of the interaction parameter. Using the -0.13 value for χ_{12}, the interaction energy density results $-9.2\ \mathrm{J/cm^3}$ at 451 K, the melting temperature of pure iPHB.

Table 1
Melting temperature of the different investigated samples

Blend composition (% iPHB)	Melting point (K)
50	444
60	445
70	447
85	449
100	450

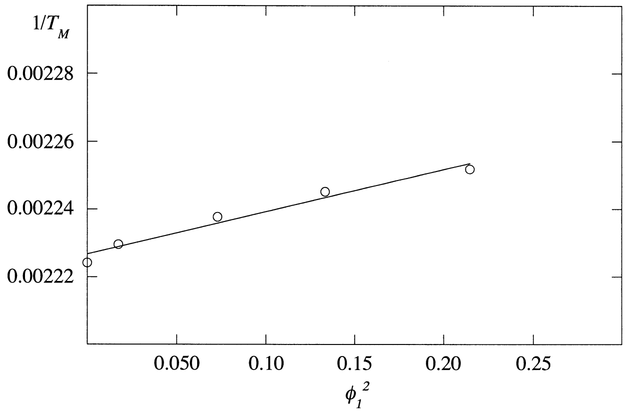

Fig. 2. Plot of the inverse of the iPHB melting temperature against the square of the volume fraction of the second component for iPHB/ECH-*co*-EO blends.

The negative values of χ_{12} and B are consistent with the macroscopic observation of the miscibility through glass transition measurements. Our values reasonably agree with the value recently reported in literature [20], which corresponds to iPHB mixtures prepared by casting from chloroform solutions. Our value is higher than that reported there ($B = -6.3\ \mathrm{J/cm^3}$), a discrepancy that could arise from the different origin of the iPHB samples. We have previously mentioned that it was impossible to dissolve completely our samples in chloroform.

3.3. Segmental interactions in the iPHB/ECH-co-EO copolymer blends. The binary interaction model

It is interesting to compare the B value above reported with that obtained for iPHB/PECH blends in a previous work [14]. The value corresponding to iPHB/PECH blend was $B = -10.4\ \mathrm{J/cm^3}$, against the $B = -9.2\ \mathrm{J/cm^3}$ value reported here for the iPHB blends with the ECH-*co*-EO copolymer. So, no strong differences are observed due to the inclusion of ethylene oxide units in the amorphous component, although the copolymer seems to be less miscible than PECH. The ethylene oxide units are expected to compete with the ether moieties of poly(epichlorohydrin) and the ester groups of iPHB (all are donor groups) in interactions with the chlorine group of the ECH unit.

These experimental results can be compared with those obtained by Fernandes et al. [33] who studied the phase diagrams of mixtures of poly(methyl acrylate) (PMA) with PECH and ECH-*co*-EO copolymers. The comparison is pertinent because of the structural similarities between iPHB and PMA. According to their phase separation data, PMA would be more miscible with PECH than with the ECH-*co*-EO copolymer, a result that seems to be consistent with those reported here for iPHB and the same second components.

In order to know more about the role of the different possible interactions in the final interaction energy density of our blends, we have used a theoretical model, which has been particularly successful in explaining the phase behaviour of polymer/copolymer blends. According to the so-called binary interaction model [34–36], the net interaction energy density, B, in mixtures of a polymer (3) with a random copolymer having 1 and 2 unities can be expressed as

$$B = B_{13}\phi_1 + B_{23}\phi_2 - B_{12}\phi_1\phi_2 \quad (3)$$

In this equation, B is a function of the different segmental interaction energy densities (B_{ij}) between the different monomers and the comonomer volume fractions (ϕ_1, ϕ_2) in the copolymer.

The B_{ij} corresponding to the different segments involved in mixtures of iPHB with random copolymers of ECH and EO can be found in the literature. Interaction energy densities for PHB and PECH have been reported by Finelli et al. [15] and by Dubini Paglia et al. [17]. Unfortunately, these results are not completely comparable. In the first case [15], interaction parameters (or energy densities) were calculated using the Nishi–Wang Eq. (1) and experimental melting points not corrected in terms of the well-known Hoffman–Weeks plots. This correction was, however, considered in the paper of Dubini Paglia et al. [17]. Trying to be consistent with the experimental interaction energies we have determined, we have preferred to use B_{ij} from papers where the Hoffman–Weeks treatment has not been considered. In this sense, Finelli et al. provided an iPHB/PECH interaction parameter of -0.23, which can be transformed in an interaction energy density of $B_{13} = -12.5$ J/cm^3, after considering Eq. (2). In this case, T is the iPHB melting point (approximately 453 K) and $V_1 = 68.03$ cm^{3}mol^{-1} [33], the PECH molar volume. iPHB/PEO interaction energy densities were also determined by Avella and Martuscelli [10] using the same methodology. From an interaction parameter of -0.075, the same melting point for iPHB and the PEO molar volume (44 cm^3 mol^{-1}), $B_{23} = -6.4$ J/cm^3. Finally, the interaction energy density for a PECH/PEO pair has been reported by Min et al. [37]. The result was $B_{12} = -3.8$ J/cm^3.

Using these data and Eq. (3), the evolution of the interaction energy density B with the copolymer composition can be easily calculated (see Fig. 3). The energy density B is always negative, varying between -12.5 and -6.4 J/cm^3, when the EO percentage in the ECH-*co*-EO copolymer is increased. Such a trend is a consequence of the concurrence of three negative segmental interaction energy densities. In other systems [34–36] where B_{12} is sufficiently negative, B can be positive in some compositions, indicating the phase separation of the mixture in these conditions.

In the specific case of the ECH-*co*-EO copolymer used in this paper (30% in weight of EO in the copolymer), the experimental value ($B = -9.2$ J/cm^3) is similar to the theoretical one ($B = -9.9$ J/cm^3, calculated at the corresponding volume fraction $\phi_{EO} = 0.34$).

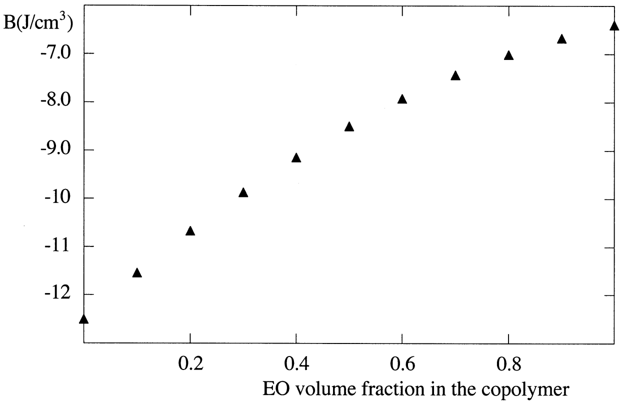

Fig. 3. Evolution of the interaction energy density in iPHB/ECH-*co*-EO blends with the EO composition in the copolymer.

3.4. Carbon dioxide sorption measurements

The CO_2 sorption kinetics recorded in the Cahn electrobalance for pure iPHB and its blends with the copolymer (ECH-*co*-EO) are very similar to that shown in Fig. 4. The weight gain (M_t) increases during the experiment up to an equilibrium value, M_∞, from which the concentration of the gas sorbed in the polymer, C, can be calculated using the following equation:

$$C\left[\frac{\text{cm}^3\ \text{STP}}{\text{cm}^3}\right] = \frac{22414 M_\infty \rho_{\text{pol.}}}{m_{\text{pol.}}\text{MW}_g} \quad (4)$$

where $m_{\text{pol.}}$ and $\rho_{\text{pol.}}$ are the mass and the density of the polymer, respectively, and MW_g is the molecular mass of the gas (44 g/mol, in the CO_2 case).

When the C values at different gas pressures p are plotted against this last variable, the CO_2 equilibrium sorption isotherms are obtained. The isotherms obtained for iPHB and its blends are qualitatively very similar to that shown in Fig. 5, which corresponds to a blend containing 60% of iPHB. All of them show nearly linear behaviours in the studied pressure range, which can be interpreted in terms of

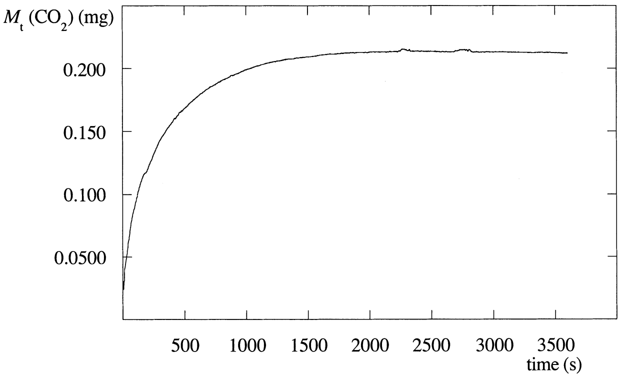

Fig. 4. CO_2 sorption kinetics in a 70/30 iPHB/ECH-*co*-EO film at 0.5 bar and 303 K.

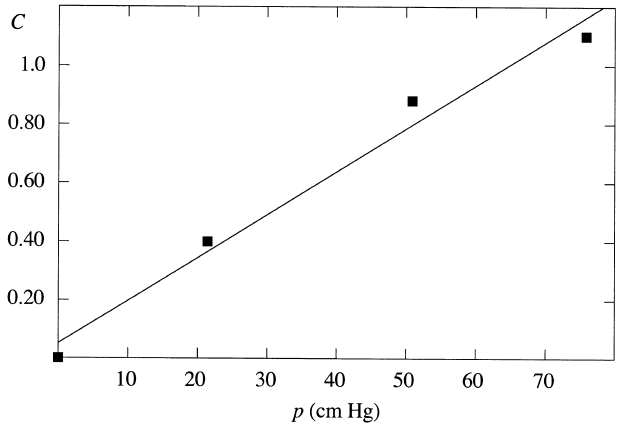

Fig. 5. Sorption isotherms for CO_2 in a 60/40 iPHB/ECH-*co*-EO blend at 303 K.

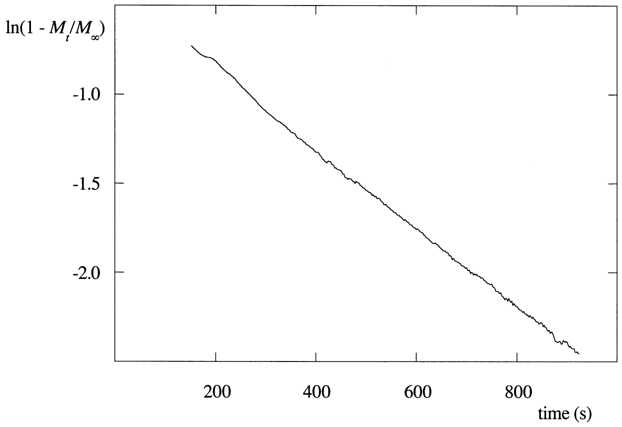

Fig. 6. Long-time plot for obtaining the diffusion coefficient of the ECH-*co*-EO copolymer at 0.5 bar and 303 K.

the Henry's law:

$$C = K_H p \tag{5}$$

where K_H is the solubility coefficient (or Henry's law constant) and p is the CO_2 applied pressure. This is the typical behaviour in rubbery polymers and mixtures as well as in semicrystalline materials with rubbery amorphous regions (as is the case of our blends). It is generally assumed that the crystalline regions are impermeable to the penetrant, which passes through the polymer film using the amorphous regions.

Using the data of sorption experiments, such as those shown in Fig. 4 but before the equilibrium situation, it is possible to extract additional information about the transport processes. The amount of the penetrant, M_t, taken up by the film in a time, t, is given [38,39] by the equation:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2}{\ell^2}t\right) \tag{6}$$

where M_∞ has been previously defined, ℓ is the film thickness and D the diffusion coefficient (in cm^2/s). This equation has been obtained by solving the differential equation corresponding to the second Fick's law and considering the same penetrant concentration (instantaneously established) at both faces of the film and without considering the effects of diffusion at the edges of the film.

For experimental long times the last equation may be approximated by:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2}{\ell^2}t \tag{7}$$

and D can be calculated from an adequate plot of the sorption data. Fig. 6 shows such a plot for the specific case of the ECH-*co*-EO pure copolymer, as representative of the rest of the investigated samples. In order to use Eqs. (4) and (7), we need both the density and the thickness of the samples. These values are summarized in Table 2. Table 2 also contains crystallinity values that will be used in the next discussion. They were measured from DSC data, using the corresponding iPHB melting enthalpies of the different blends and the ΔH_M value of a 100% crystalline pure iPHB obtained by extrapolation [32].

Diffusion coefficients for the different polymers and blends obtained following the method outlined in the previous paragraphs are summarized in Table 3.

At the steady state and when the diffusion coefficient is independent of the penetrant concentration, the permeability coefficient can be written as the product of the effective diffusion, D, and solubility, S, coefficients:

$$P = DS \tag{8}$$

In samples following the Henry's law, the constant K_H and the S coefficient are equivalent forms of expressing the same magnitude. The obtained P results are also summarized in Table 3.

As it can be seen, the CO_2 sorption and permeability increase with the amount of ECH-*co*-EO copolymer added to iPHB. This was the expected behaviour by different reasons. First, the effect of the copolymer is to decrease the global crystallinity of the blend, having more amorphous polymer available to the sorption of the CO_2 molecules. As previously mentioned, we are assuming zero gas solubility in the crystalline phase. Second, it is clear that the pure ECH-*co*-EO copolymer is much more permeable to carbon dioxide (less barrier character) than iPHB. This high permeability arises from high values of the CO_2 solubility and diffusivity in this rubbery material.

Although decreasing the barrier character of the pure

Table 2
Values of density, thickness and crystallinity of the different samples investigated in sorption measurements

Blend composition (% iPHB)	Density (g/cm^3)	Thickness (μm)	X_c (%)
100	1.2433	43.6	66.7
85	1.2478	46.5	61.5
70	1.2546	41.9	50.4
60	1.2601	63.4	43.4
0	1.2700	143.0	0

Table 3
Transport properties of iPHB/(ECH-*co*-EO) blends at 303 K and 0.5 bar

Blend concentration (% w/w iPHB)	Diffusion ($D \times 10^8$) (cm^2/s)	Solubility ($S \times 10^2$) cm^3/(cm^3 cm Hg)	Permeability P (Barrer)
0	5.7	19.1	109.2
60	4.3	5.4	23.2
70	1.9	3.9	7.6
85	1.5	3.4	4.9
100	0.1	1.1	0.1

iPHB, the addition of limited amounts of the ECH-*co*-EO copolymer provides new materials with permeabilities comparable to those of other materials used in this type of applications.

3.5. Interactions and sorption data

From the Flory–Huggins solution theory for ternary systems in equilibrium, the solubility coefficient of a penetrant in a polymer blend can be related to the solubility coefficients in the pure component by [40]:

$$\ln K_{\mathrm{H}} = \phi_1 \ln K_{\mathrm{H1}} + \phi_2 \ln K_{\mathrm{H2}} + \left(\frac{BV_3}{RT}\right)\phi_1\phi_2 \qquad (9)$$

K_{H} is the Henry's law or solubility constant in the miscible blend and K_{H1} and K_{H2} are the corresponding constants for the pure polymers, ϕ_1 and ϕ_2 are the volume fractions of the two polymers in the blend and V_3 is the molar volume of CO_2 in the condensed state, which has been estimated to be 55 cm^3/mol. Thus, Eq. (9) can be used to simulate the behaviour of the solubility coefficient of carbon dioxide in PHB/ECH-*co*-EO blends as a function of the polymer concentration if the interaction energy density for the polymer pair B is known. We will use the value obtained from melting point depression measurements.

In order to use adequately Eq. (9) in blends of an amorphous and a semicrystalline component (where the crystalline phase is impermeable to the penetrant), the solubility coefficient (or Henry's law constant) has to be referred to the concentration of the polymers in the amorphous phase. Consequently, the volume fractions ϕ_1 and ϕ_2 in Eq. (9) have been calculated on an amorphous basis, assuming that the ECH-*co*-EO chains are rejected into the amorphous phase during the iPHB spherulite growth period [6]. Consequently, the different blends may be considered as mixtures of pure iPHB crystals and a homogeneous miscible blend of uncrystallized iPHB and ECH-*co*-EO chains.

In a particular polymer or copolymer film, the CO_2 solubility coefficient in the amorphous phase, $K_{\mathrm{H}}^{\mathrm{am}}$, required in applying Eq. (9), can be calculated from the experimental value K_{H}, as:

$$K_{\mathrm{H}}^{\mathrm{am}} = \frac{K_{\mathrm{H}}}{\phi_{\mathrm{am}}} \qquad (10)$$

where ϕ_{am} is the volume fraction of amorphous material in the film.

The copolymer volume fraction in the amorphous phase, ϕ_1, can be calculated by:

$$\phi_1 = \frac{\omega_1/\rho_1}{\dfrac{1}{\rho_{\mathrm{B}}} - \dfrac{(X_{\mathrm{c}}/100)}{1.279}} \qquad (11)$$

where ω_1 is the weight fraction of the ECH-*co*-EO copolymer in the blend, ρ_1 is the copolymer density, X_{c} is the iPHB crystallinity, ρ_{B} is the blend density and 1.279 corresponds to the extrapolated density (in g/cm^3) of a 100% crystalline PHB. The iPHB volume fraction in the amorphous phase will be $\phi_2 = 1 - \phi_1$.

Using the different $K_{\mathrm{H},i}^{\mathrm{am}}$ and ϕ_i in Eq. (9) and the value of $B = -9.2$ J/cm^3 it is possible to obtain a theoretical dependence of the solubility parameter of carbon dioxide ($K_{\mathrm{H}}^{\mathrm{am}}$) in the blends with the concentration of these blends. Fig. 7 summarizes these calculations together with the experimental results. Although the agreement looks reasonably good, it should be considered that the term containing the interaction energy density in Eq. (9) has a minor influence in the value of K_{H} than the two other terms. So, substantial variation in the B value does not change drastically the fitting of the experimental results. In fact, if Eq. (9) and K_{H} values of the pure components and their blends are used to calculate B at every concentration of the blend the average was 5.3($\pm$2.4) J/cm^3. This calculation illustrates the intrinsic difficulty in obtaining interaction

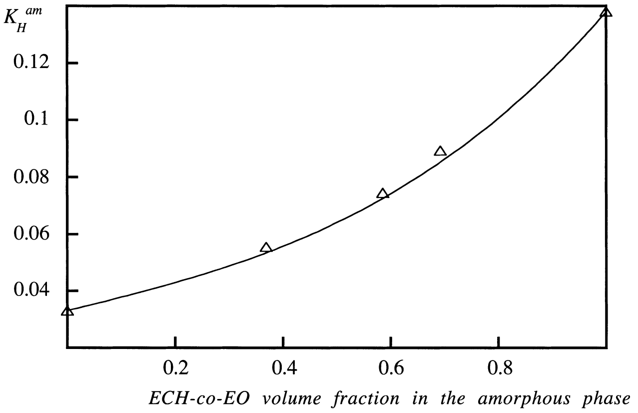

Fig. 7. Fitting of CO_2 sorption data in the PHB/ECH-*co*-EO mixtures. The curve is calculated with Eq. (9) and $B = -9.2$ J/cm^3.

energy densities from solubility data of a penetrant in polymer blends.

But, in comparing this average value with the B value obtained by melting point depression, we have to remember that the theoretical and experimental values used in Fig. 7 are obtained at very different temperatures. Sorption data were taken at 303 K and the blend melting points are in the vicinity of 443 K. It is well known that the interaction parameter (and the interaction energy density) is temperature dependent [41].

4. Conclusions

iPHB and ECH-*co*-EO copolymer blends are miscible over the whole composition range. The interaction parameter obtained from melting point depression analysis was -0.13 whereas, the corresponding interaction energy resulted -9.2 J/cm^3. Our data are in good agreement with data reported recently in literature [20]. The miscibility has been explained on the basis of the competition of the different segmental interactions occurring between the functional groups involved in iPHB and the copolymer.

The paper also summarizes the solubility, diffusivity and permeability of carbon dioxide in iPHB/ECH-*co*-EO blends containing up to 40% of the ECH-*co*-EO copolymer, as potential biodegradable materials in packaging and barrier applications. As it can be seen in Table 3, the incorporation of a 40% ECH-*co*-EO copolymer increases substantially the gas permeability. Two concurrent effects determine this behaviour: the increasing of the penetrant solubility and the increasing of its diffusivity. Although the barrier capacity of these blends is substantially diminished with respect to that of the pure iPHB, the permeability values at low ECH-*co*-EO copolymer concentrations are in the range of other polymeric materials used in packaging applications.

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