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Polymer 43 (2002) 6205–6211

polymer

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Miscibility and carbon dioxide transport properties of blends of bacterial poly(3-hydroxybutyrate) and a poly(vinylidene chloride-*co*-acrylonitrile) copolymer

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Received 15 May 2002; received in revised form 15 July 2002; accepted 16 July 2002

Abstract

The purpose of this work is to study the CO_2 transport properties of isotactic poly(3-hydroxybutyrate) (iPHB) blended with a miscible second component, a copolymer of vinylidene chloride (VDC) and acrylonitrile (AN) units. All the investigated blends are rubbery, allowing a reasonable strategy to tough PHB without impairing its original biodegradability. The miscibility required for this purpose was confirmed by differential scanning calorimetry, measuring both the glass transition and melting temperatures of the blends. The melting point depression induced by the copolymer was used to quantify the interactions between the components of the blend. Carbon dioxide transport properties of blends having less than 50% by weight of the copolymer were measured by gravimetric sorption experiments in a Cahn electro balance. The effect of the VDC-*co*-AN copolymer was to decrease the diffusivity and permeability of the pure iPHB due to its well-known high barrier character. © 2002 Published by Elsevier Science Ltd.

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

1. Introduction

Bacterial polyhydroxyalkanoates (PHAs) have received much attention in the last decade owing to their biodegradability, biocompatibility and natural origin. They have been used in different applications in important commercial fields such as medicine, agriculture and packaging [1,2].

The most studied member of this family is poly(3-hydroxybutyrate), which is biosynthesised by a large number of bacteria as intracellular carbon and energy sources. It is an isotactic high molecular weight polymer with a melting point around 450 K, and a glass transition close to 278 K.

iPHB shows a high barrier behaviour to permeant gases such as O_2 or CO_2. However, its application in the package domain presents some problems related to its difficult processing (thermal degradability at temperatures not far above the melting point), low elongation at break (high fragility) and its high production cost [3,4]. In order to confront these difficulties, three different strategies have been developed: (a) copolymerisation with other alkanoates, (b) addition of biodegradable plasticizers and (c) blending with a second polymer.

Concerning the copolymerisation, several kinds of PHA copolymers have been described in the literature, incorporating additional structural units such as 3-hydroxyvalerate, 4-hydroxybutyrate, or 3-hydroxyhexanoate [4]. These materials offer an improvement of both mechanical and thermal properties, by incorporating flexible units in the main chain of the polymer and decreasing the melting point, so avoiding the thermal degradation.

The second proposed way is the addition of different low molecular additives, as is the case of a PHB sold under the trade name of Biomer, which incorporates a biodegradable citrate as a plasticizer. Although this addition improves both mechanical properties and price, it provokes a substantial decrease in the barrier properties against atmospheric gases.

The other main alternative to achieve these goals implies to form blends with an adequate second polymer. Many

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PII: S0032-3861(02)00493-7

immiscible iPHB based blends have been described in the literature as, for example, those containing polystyrene [5], poly(methylmethacrylate) [6] or ethylene-vinylacetate copolymers [7,8]. On the other hand, a large number of polymers form miscible blends with iPHB, as is the case of poly(vinylphenol) [9–11], poly(vinylacetate) [12,13], poly(epichlorohydrin) [14–16], synthetic (atactic) PHB [4, 16] and poly(ethylene oxide) [17–20]. But, in some of these blends, some properties that change after incorporating the second polymer show undesirable side effects. For example: blending iPHB with PEO led to a loss of the water resistance of the pure iPHB, a property that is desirable to be retained for most applications. In other systems, like iPHB/cellulose acetate butyrate blends [21], the biodegradability is lost due to restrictions in the PHB segmental mobility in the blend amorphous phase. It appears that this segmental mobility is a very important prerequisite for improving or retaining the iPHB biodegradation capability in its miscible blends.

This condition can be more easily achieved when rubbery polymers are used as second components [15] as is the case of a vinylidene chloride (VDC) and acrylonitrile (AN) copolymer. Although the glass transition temperature of the copolymer is above the room temperature, miscible blends with iPHB (with a T_g of 278 K) have glass transition temperatures in the vicinity of the room temperature. For instance, Lee et al. [22] have described a miscible mixture of a 80:20 VDC–AN copolymer with PHB. Up to compositions containing 80% of the copolymer, the glass transition temperature of the blend remains below the room temperature, the adequate conditions for iPHB biodegradability to occur.

Copolymers of VDC and AN are known to have excellent barrier properties to atmospheric penetrant gases. Thus, the aim of the present work is the study of the modification of the iPHB transport properties when a VDC-*co*-AN copolymer is incorporated. As representative penetrant we have selected carbon dioxide. Moreover, the addition of the VDC-*co*-AN copolymer will presumably improve other iPHB mechanical properties given the increase of the elastomeric contents of the mixtures with respect to that of the pure iPHB. This behaviour has been previously found in blends of iPHB with other rubbery materials [14].

2. Experimental section

2.1. Materials

Bacterial iPHB was obtained from Biomer, Germany. The average molecular weights were $\bar{M}_n = 220\,000$ g/mol and $\bar{M}_w = 374\,000$ g/mol (referred to polystyrene calibration standards), as determined by SEC-GPC at 303 K using chloroform as solvent.

The copolymer of vinylidene chloride and acrylonitrile was a Dow product, sold under the trade name of Saran F220. It contained a 32% mole percent of AN, as determined by ^{13}C NMR (Varian 200 spectrometer) in DMSO. Its glass transition temperature was 328 K.

For the purpose of confirming the blend miscibility, another bacterial iPHB, from a different commercial origin (Aldrich) has been used. Its weight average molecular weight was 437 000 g/mol.

As an additional test of the complete miscibility between our copolymer and the amorphous regions of the bacterial PHB, blends of the VDC–AN copolymer with a synthetic atactic PHB (aPHB) were also prepared. aPHB was synthesised by ring opening polymerisation of DL-β-butyrolactone in toluene solution at 313 K, using a modification of the Et_2Zn/H_2O initiator described in the literature [23]. 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 $\bar{M}_n = 122\,000$ g/mol and $\bar{M}_w = 233\,000$ g/mol (referred to polystyrene calibration standards). The isotactic dyad fraction of the produced polymer was 0.45, as determined by ^{13}C NMR.

2.2. Blend preparation

Different methods were used to prepare the different required blends. Blends of the copolymer with aPHB were prepared by solution/precipitation in THF/*n*-hexane. Blends containing bacterial PHB (Aldrich), only prepared to confirm the miscibility of the mixture, were also prepared by solution/precipitation using epichlorohydrin at reflux as solvent and cold *n*-hexane (or a cold mixture of *n*-hexane and diethyl ether) as precipitant.

In order to obtain adequate films to the experiments carried out in the Cahn electrobalance, the blends were prepared in a different manner. The iPHB (Biomer), and the copolymer were premixed in the desired compositions (0, 50, 60, 70, 85 and 100% w/w of the first component), by a solution/precipitation method, using epichlorohydrin at reflux as solvent and cold hexane as precipitant. The premixed samples were stored for 4 days under vacuum and 373 K for a complete removal of the solvents. Then, they were compression moulded in a Graseby Specac hot press at 458 K for 2 min under a pressure of 2 ton/m^2. After this process, the mould was transferred to the water-cooling unit attached to the press, so allowing the crystallisation of the iPHB. The films so obtained were stored other four days under vacuum and 373 K for removing possible residual traces of solvent. They were stored under vacuum and room temperature, before the sorption experiments were performed. These blends were also calorimetrically tested in order to determine their transition temperatures and crystallinities.

2.3. Methods

Thermal analysis was performed in a Perkin–Elmer

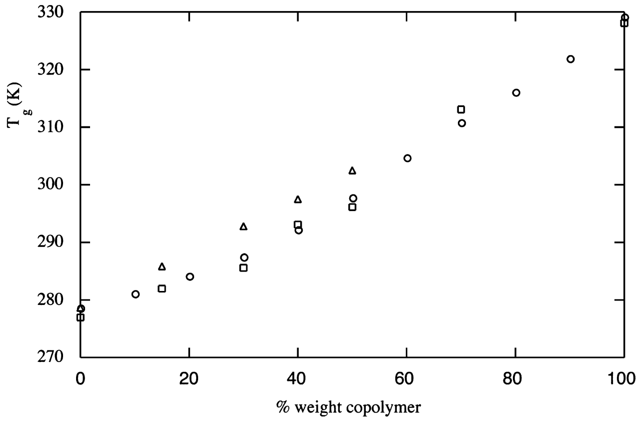

Fig. 1. Glass transition temperatures of iPHB/VDC-*co*-AN blends: iPHB (Aldrich)/copolymer blends prepared by solution/precipitation in epichlorohydrin/*n*-hexane/ethyl ether (○) or in epichlorohydrin/*n*-hexane (□). iPHB (Biomer)/copolymer blends prepared by solution/precipitation in epichlorohydrin/*n*-hexane (△).

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

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. Thickness was measured by a Duo Check gauge. An average value 40 μm (± 1 μm) was obtained in all samples.

Carbon dioxide sorption experiments were performed in a Cahn D-200 electro balance enclosed in a thermostated box at 303 K. After hanging up a polymer film into the balance sorption chamber, it was evacuated overnight. Carbon dioxide was then admitted in the balance at different sub-atmospheric pressures, and the weight change of the sample was recorded. The sorption curves were corrected by subtracting a blank run, obtained under the same conditions but without sample.

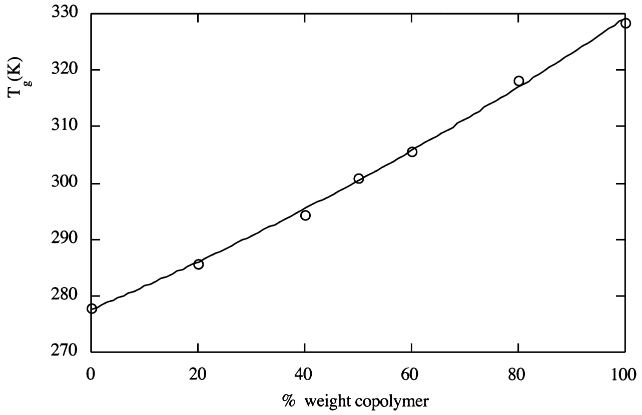

Fig. 2. Glass transition temperatures of blends of aPHB and the VDC/AN copolymer prepared by solution/precipitation in THF/*n*-hexane.

3. Results and discussion

Because of the high insolubility of iPHB in conventional solvents, mixtures of the bacterial PHB and the copolymer have only one efficient common solvent: epichlorohydrin. However, cast films from these solutions were difficult to dry and evidenced clear symptoms of heterogeneity, probably due to some kind of $\Delta\chi$ effect during the drying process. However, blends prepared by solution/precipitation, as described in Section 2.2, had a more repetitive behaviour.

Glass transition temperatures (T_g) of the different investigated blends of bacterial iPHB are resumed in Fig. 1. Data are consistent with a complete miscibility of iPHB and the VDC-*co*-AN copolymer over the whole range of compositions. The presence of a single T_g between those of the pure components suggests the existence of a single homogeneous amorphous phase, irrespective of the iPHB origin (Aldrich or Biomer) and of the blend preparation method.

This result was also confirmed by the similar behaviour observed in blends of the copolymer with a 100% amorphous aPHB. Data are shown in Fig. 2.

Table 1 contains the melting points (T_M) and crystallinity degrees (X_c) of the samples that will be used in the measurements of the carbon dioxide transport properties. The crystallinity degree was calculated using the iPHB ΔH of fusion in the mixtures, measured by DSC, and the extrapolated value corresponding to a 100% crystalline iPHB [24]. Crystallinity is an important parameter in comparing solubility coefficients, given that only the amorphous regions are accessible to the gas penetrant.

Crystallinities in Table 1 are referred to the total mass of the blend sample. When these data are used to calculate the crystallinity of the iPHB contained in the blend a slow but progressive decrease from 68.6 to 60.0% is observed in going from the pure iPHB to the 50/50 blend. This capacity of iPHB in crystallizing even in the presence of substantial

Table 1
Thermal properties of iPHB and its blends with VDC-*co*-AN copolymer used in transport properties experiments

iPHB (%w/w)	T_M (K)	X_C (%)
100	449.6	68.6
85	449.2	54.5
70	448.5	45.8
60	447.6	34.9
50	446.1	30.0

X_c is referred to global mass of the blend.

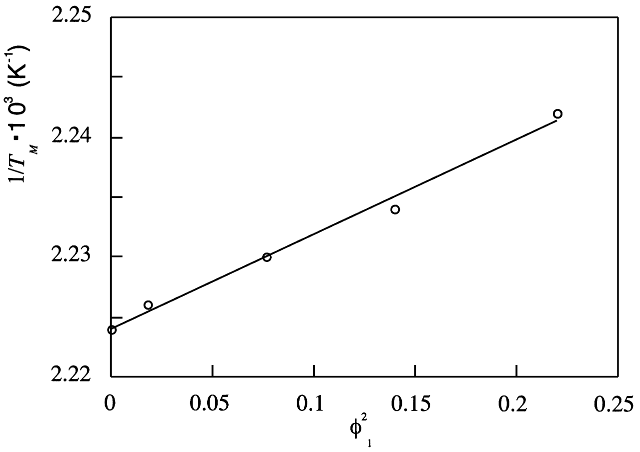

Fig. 3. Inverse melting temperature versus square of the amorphous phase fraction in iPHB/VDC-*co*-AN copolymer blends.

amounts of a rubbery miscible second component has been previously observed [15,16].

The observed decrease in the melting temperatures allows calculating the polymer–polymer Flory–Huggins interaction parameter, following the Nishi–Wang treatment [25]. According to it, polymer–polymer interaction parameters can be calculated from the depressions in the melting point of a crystalline polymer due to the presence of a second amorphous component at different concentrations. Data are used in the equation

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

where T_{M} and T_M^0 are the melting temperatures of the crystallisable polymer in the blend and in the pure state, respectively, V_1 and V_2 are the molar volumes of the repeating units of the amorphous and crystalline polymers, ΔH_2 is the melting enthalpy of the 100% pure crystalline phase per mole of repeating unit, ϕ_1 is the volume fraction of the uncrystallisable polymer, and χ_{12} is the Flory–Huggins interaction parameter between the blend components.

Fig. 3 shows the well-known Nishi–Wang plot for determining interaction parameters from melting point depression data. From the slope of this plot, a value for the interaction parameter of -0.08 was calculated. In this calculation, the following required parameters were used: $\Delta H_2 = 3001$ cal/mol [24], $V_1 = 61.25\ \mathrm{cm}^3/\mathrm{mol}$ [26] and $V_2 = 68.03\ \mathrm{cm}^3/\mathrm{mol}$ [27]. The negative value is consistent with a miscible blend system. A significantly higher value of the interaction parameter (-0.27) has been reported by Lee et al. [22] with a very similar VDC-*co*-AN copolymer, using the Hoffman–Weeks plot. Although the differences could be attributed, in a first instance, to the use or not of the Hoffmann–Weeks plots, it is necessary to point out that, in spite of its well-founded character, results from extrapolations such as those of the HW plots are subjected to large confidence intervals. In fact, in other PHB blends, the interaction parameter with or without the HW treatment is quite similar. For instance, in previous papers of PHB/poly(epichlorohydrin) blends, data from Finelli et al. [15] and others from our own group [16], without considering HW plots, are similar to those obtained by Dubini Paglia et al. [14] who have considered the morphological effects.

The interaction energy density, B is a different form to express the Flory–Huggins interaction parameter

$$B = \frac{RT\chi}{V_{\mathrm{r}}} \qquad (2)$$

eliminating the use of a reference volume (V_{r}), usually the molar volume of the amorphous component V_1. B values are given in cal/cm^3, allowing an easier comparison of interactions between different functional groups. The interaction energy density between PHB and the AN–VDC copolymer was calculated using Eq. (2). The result was $B = -1.2\ \mathrm{cal/cm}^3$.

As a way of knowing more about the interactions that stabilize the different investigated mixtures, we have used the so-called binary interaction model that has been particularly successful in explaining the behaviour of polymer/copolymer blends [28–30].

According to this model, the net interaction energy density, B, in mixtures of a polymer (3) with a random copolymer of unities 1 and 2 can be expressed as

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

a function of the different interaction energy densities (B_{ij}) between the monomers i and j and the comonomer volume fractions (ϕ_{ij}) in the copolymer.

It is not easy to find B_{ij} values corresponding to the different segments involved in our case, so we have preferred to use interaction energy densities for different segmental pairs calculated by Gan et al. [31], according to the Lattice Fluid Theory. We have assumed that interactions of VDC are very similar to those of vinyl chloride and that interactions of HB units should be very similar to other ester or acrylate units. In this sense, B_{23} (segmental interaction between HB and AN units) has been taken as 4.6 cal/cm^3, B_{12} (segmental interaction between VDC and AN units) should be of the order of 4.2 cal/cm^3 and, finally, the interaction between VDC and HB units (B_{13}) should be -1.0 cal/cm^3 or less, given the values reported for blends of a copolymer of VDC and VC with polyacrylates and polymethacrylates [32,33].

Using these data and Eq. (3), the evolution of the B term with the VDC volume fraction in the copolymer can be calculated (Fig. 4). B is considered independent of the composition of the blend. As it can be seen, the binary interaction model agrees with the experimental data in the sense that copolymers with high content of VDC should be miscible with PHB, although the interaction level is not very high. Even the calculated value (-0.28 cal/cm^3) for a copolymer containing 68% of VDC units (the corresponding

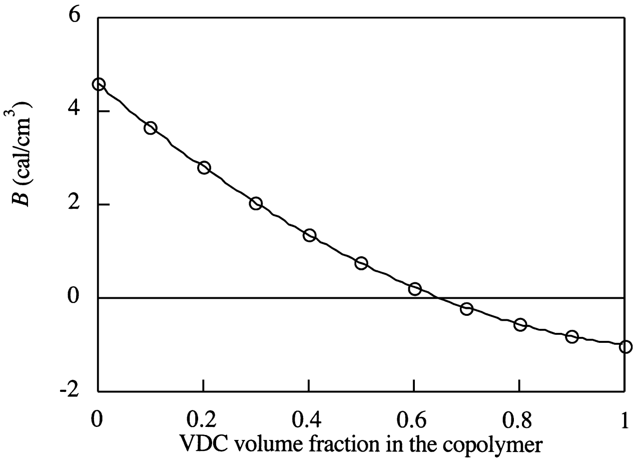

Fig. 4. Evolution of the interaction energy density with the VDC composition in the copolymer.

VDC volume fraction is 0.72) is in reasonable agreement with that calculated using the Nishi–Wang treatment.

3.1. Carbon dioxide sorption measurements

A typical gas sorption experiment is illustrated in Fig. 5. The weight gain tends to an asymptotic value denoted as M_∞, the equilibrium weight of gas dissolved in the polymer film. This equilibrium situation is also expressed in the form of a concentration of the gas (in standard conditions) per volume unit of the polymer

$$C\left[\frac{\mathrm{cm^3STP}}{\mathrm{cm^3}}\right] = \frac{22\,414\, M_\infty \rho_{\mathrm{pol}}}{m_{\mathrm{pol}} MW_{\mathrm{g}}} \tag{4}$$

where M_∞ is equilibrium weight gained by a polymer sample of a mass m_{pol} and density ρ_{pol} during the sorption experiment and MW_{g} is the molecular weight of the gas (44 g/mol, in the CO_2 case).

Carbon dioxide equilibrium sorption isotherms (plots of C against the applied pressure) at 303 K for iPHB and its blends are qualitatively very similar to that presented in Fig. 6. All of them show a linear behaviour in the studied pressure range, a behaviour which can be interpreted in terms of the Henry's law, which states the proportionality between the pressure exercised by the penetrant p and the gas concentration finally sorbed in the polymer.

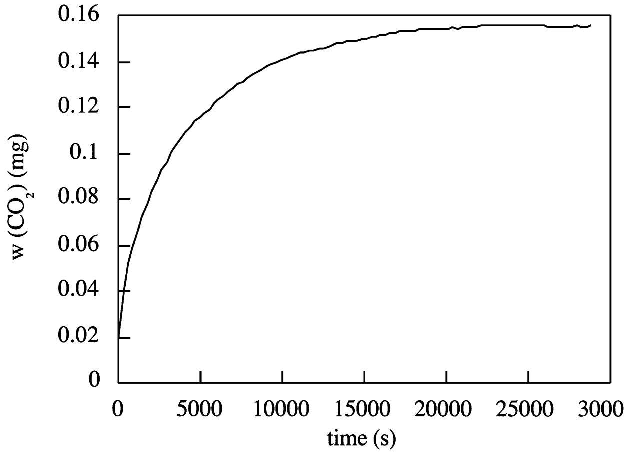

Fig. 5. CO_2 sorption kinetics at in the 70/30 iPHB/VDC-*co*-AN copolymer membrane at 0.5 atm and 303 K.

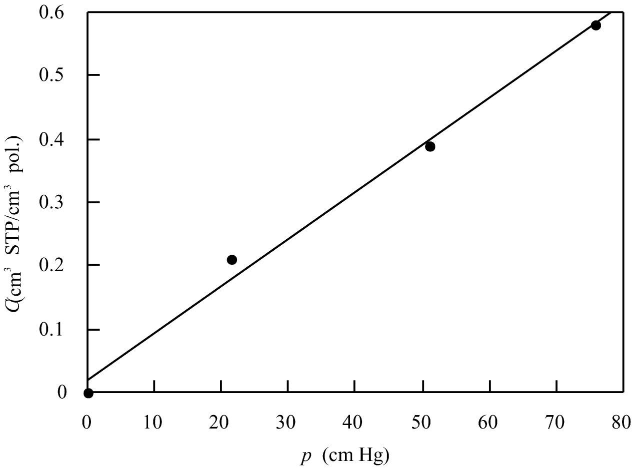

Fig. 6. CO_2 sorption isotherms in iPHB/VDC-*co*-AN 85:15 copolymer blend at 303 K.

$$C = K_{\mathrm{H}} p \tag{5}$$

K_{H} is the Henry coefficient (also called solubility coefficient and denoted by S).

Using the data of sorption curves such as Fig. 5 before reaching the equilibrium situation, the amount of the diffusant, M_t, taken up by the sheet in a time, t, is given by Eq. (6) [34,35]

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

where M_∞ has been previously defined, l is the film thickness and D the diffusion coefficient (in cm^2/s). This equation can be obtained by solving the differential equation corresponding to the second Fick's law after considering the

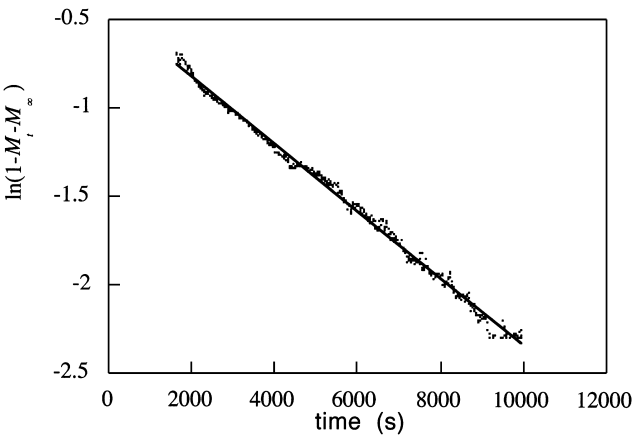

Fig. 7. Plot according Eq. (7) for calculating the diffusion coefficient of a 70/30 iPHB/VDC-*co*-AN copolymer membrane at 0.5 atm and 303 K.

Table 2
Transport properties of the different investigated polymers and blends at 303 K and a CO_2 pressure of 0.5 atm

iPHB content (%w/w)	Diffusivity, D ($\times 10^9$ cm^2/s)	Solubility, S ($\times 10^2$ cm^3/cm^3 cm Hg)	Permeability P (Barrer)
100	1.19	1.14	0.13
85	0.79	3.14	0.25
70	0.50	1.88	0.094
60	0.15	2.60	0.039
50	0.11	2.33	0.027

same concentration at both faces of the film (which is established instantaneously) and without taking into account the effects of diffusion at the edges of the film. For long times, the last equation may be approximated by:

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

The diffusion coefficient D can be calculated from the slope of an adequate plot of the sorption data (Fig. 7).

At the steady state and when diffusion coefficient is independent of the penetrant concentration (as is our case in the limited range of sub-atmospheric pressures investigated), the permeability coefficient of a membrane can be written as the product of the diffusion coefficient D and the solubility coefficient S:

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

In our case S is identical to the Henry's law coefficient K_H included in Eq. (5). Data of solubility, diffusivity and permeability are summarized in Table 2.

The diffusion coefficients decrease with the addition of the copolymer because of its intrinsic higher barrier character. Moreover, the glass transition temperature of the blends increases when the copolymer composition in the blend increases. This would affect the mobility of the amorphous region at room temperature, restricting the transport of the penetrant molecules. However, it is also necessary to point out the fact that the data of the pure copolymer would correspond to the glass state, whereas the blends are clearly rubbery at 303 K. The permeability value for the pure copolymer was taken from literature [36] ($P = 0.029$ Barrer). Because of the high barrier character of the copolymer, the equilibrium CO_2 weight values of our sorption experiments were within the experimental error of our balance.

Consequently, the observed values for the blends seem to exhibit a synergistic effect, as far as the permeability is concerned. This would be probably due to a negative excess volume in the blends, as usually happens in miscible blends with specific interactions. Table 3 shows the experimental densities of the pure components and the blends.

Using the iPHB crystallinities (Table 1) in the different blends, it is possible to calculate the additive density of each composition, using those of iPHB, aPHB and VDC-*co*-AN. Results are also included in Table 3. The comparison between these densities and those experimentally measured should give us an idea about the excess volumes in the blends. In general, blends exhibit a negative excess volume. For instance, for a 60/40 blend the additive density was 1.286 g/cm^3, lower than the experimental one (1.291 g/cm^3). This implies an experimental specific volume lower than the additive one. The same happens with the other compositions, although the evolution of the excess volume with the composition has not the usual parabolic form with a minimum, probably due to the problematic blend preparation. Except in the case of the 85/15 blend experimental densities are consistent with the crystallinity degrees obtained by DSC.

Although (Table 2) the solubility coefficient seems to exhibit a more erratic behaviour with the composition of the blend, it should be taken into account that in calculating S we have used the total mass of the polymer exposed to the penetrant. However, only the amorphous regions are able to incorporate the gas. Consequently, the true solubility of the gas should be calculated using the mass of the amorphous part of the blend. When this calculation is done, (Table 4), the solubility remains almost constant except in the case of the blend 85/15, which exhibits a higher solubility than expected. This result has been repeatedly obtained and the only possible explanation could be some kind of degradation induced during the preparation of the blends. This degradative process would have also affected the expected density.

The global effect on the permeability is controlled by the composition in VDC-*co*-AN, although a clear synergistic effect is evidenced by the data of Table 2, mainly derived from the same effect in the diffusion data, as previously discussed.

Table 3
Experimental and additive densities (g/cm^3) of iPHB/VDC-*co*-AN blends. The density of the aPHB is also included for the discussion detailed in the text

	iPHB	aPHB	85/15 blend	70/30 blend	60/40 blend	50/50 blend	VDC/AN copolymer
Density (exp.)	1.243	1.170	1.254	1.276	1.291	1.306	1.418
Density (additive)			1.229	1.271	1.286	1.306	

Table 4
CO_2 solubility coefficients for iPHB and its blends with AN-*co*-VDC calculated on the basis of the amorphous PHB contents

iPHB content (%w/w)	X_c (%)	S ($\times 10^2$cm^3/cm^3 cm Hg)
100	66.7	3.42
85	54.5	6.90
70	45.8	3.47
60	34.9	3.99
50	30.0	3.33

4. Conclusions

Blends prepared by mixing iPHB and a VDC-*co*-AN copolymer containing 32% mole percent of AN units are miscible over the whole composition range. The blends showed a single glass transition temperature, and a clear iPHB melting point depression. The interaction parameter obtained from melting point depression analysis was -0.08. The corresponding interaction energy density takes a value of -1.2 cal/cm^3. The miscibility is probably conditioned by dipole–dipole interaction between the carbonyl group of iPHB and chloride atoms of VDC-*co*-AN copolymer.

The solubility, diffusivity and permeability of carbon dioxide are reported for iPHB blends containing up to 50% of the VDC-*co*-AN copolymer. As can be seen in Table 2, the incorporation of a 50% VDC-*co*-AN copolymer has the effect of decreasing the gas permeability close to the value of the pure VDC-*co*-AN copolymer (0.029 Barrer [36]). The low gas permeabilities of the investigated blends mainly arise from the substantially lower diffusivity values.

Acknowledgments

Financial support of the University of the Basque Country (project 203.215-13519/2001) and MCYT (project MAT98/0530) is gratefully acknowledged. A.G. thanks the AECI for a PhD grant.

References

[1] Chang BH. Polym News 1997;22:307.

[2] Fujimaki T. Polym Degrad Stab 1998;59:209.

[3] Grassie N, Murray EJ. Polym Degrad Stab 1984;6:95.

[4] Crespo OM. PhD Thesis. University of the Basque Country, San Sebastián, Spain; 1999.

[5] Dave PB, Gross RA, McCarthy SP. ANTEC Soc of Plastics Engrs 1990;1439.

[6] Dave B, Parikh M, Reeves MS, Gross RA, McCarthy SP. Polym Mater Sci Engng 1990;63:726.

[7] Siciliano A, Seves A, De Marco T. Macromolecules 1995;28:8065.

[8] Gassner F, Owen AJ. Polymer 1992;33:2508.

[9] Xing P, Dong L, An Y, Feng M, Avella M, Martuscelli M. Macromolecules 1997;30:2726.

[10] Iriondo P, Iruin JJ, Berridi MJ. Polymer 1995;36:3235.

[11] Coleman MM, Painter PC. Specific interactions and the miscibility of polymer blends. Lancaster, PA: Technomic; 1991.

[12] Greco P, Martuscelli E. Polymer 1989;30:1475.

[13] Hay JN, Sharma L. Polymer 2000;41:5749.

[14] Dubini Paglia E, Beltrame PL, Canetti M, Seves A, Marcandalli B, Martuscelli E. Polymer 1993;34:996.

[15] Finelli L, Sarti B, Scandola M. J Mater Sci Pure Appl Chem 1997; A34:13.

[16] Miguel O, Egiburu JL, Iruin JJ. Polymer 2001;42:953.

[17] Avella M, Martuscelli E. Polymer 1988;29:1731.

[18] Avella M, Greco P, Martuscelli E. Polymer 1991;32:1647.

[19] Avella M, Martuscelli E, Raimo M. Polymer 1993;34:3234.

[20] Kumagai Y, Doi Y. Polym Degrad Stab 1992;35:87.

[21] Tomasi G, Scandola M. J Macromol Sci Pure Appl Chem 1995;A32: 671.

[22] Lee JC, Nakajima K, Ikehara T, Nishi T. J Polym Sci, Part B: Polym Phys 1997;35:2645.

[23] Adostini DE, Lando JB, Reid Shelton J. J Polym Sci, Part A 1971;9: 2775.

[24] Sánchez-Cuesta M, Martínez-Salazar J, Barker PA, Abraham PJ. J Mater Sci 1992;23:5335.

[25] Nishi T, Wang TT. Macromolecules 1975;8:909.

[26] Hsu WP, Yeh ChF. J Appl Polym Sci 2000;75:1313.

[27] Ma M, Chen C, Hew-Der W, Chu PP, Han-Thing T. Macromolecules 1997;30:5443.

[28] Kambour RP, Bendler JT, Bopp RC. Macromolecules 1983;16:753.

[29] Paul DR, Barlow JW. Polymer 1984;25:847.

[30] Brinke G, Karasz FE. Macromolecules 1994;17:815.

[31] Gan PP, Paul DR, Padwa AR. Polymer 1994;35:1487.

[32] Woo EM, Barlow JW, Paul DR. J Polym Sci, Polym Symp 1984;71: 137.

[33] Fernandez AC, Barlow JW, Paul DR. J Appl Polym Sci 1986;29:6073.

[34] Crank J, Park GS. Diffusion in polymers. London: Academic Press; 1968.

[35] Crank J. The mathematics of diffusion, 2nd ed. Oxford: Clarendon Press; 1975.

[36] Mark HF, Bikales NM, editors. Encyclopedia of polymer science and technology, vol. 1. New York: Wiley; 1976.