# Carbon Dioxide Sorption and Diffusion in Poly(3hydroxybutyrate) and Poly(3-hydroxybutyrate-*co*-3hydroxyvalerate)

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ABSTRACT: CO<sub>2</sub> sorption and diffusion in poly(3-hydroxybutyrate) and three poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) copolymers were investigated gravimetrically at temperatures from 25° to 50°C and pressures up to 1 atm. The sorption behavior proved to be linear for all the copolymers studied. An additional set of measurements performed in a pressure decay apparatus at 35°C showed that the linearity could be extrapolated to pressures up to 25 atm. The sorption results obtained from both techniques were in good agreement. The poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) sorption kinetics were increasingly non-Fickian at the higher temperatures, thus preventing the calculation of diffusion coefficients above 35°C. Interestingly, this was not the case for poly(3-hydroxybutyrate), and diffusion coefficients and permeabilities could be calculated at all of the investigated temperatures. The 35°C permeabilities were fairly low, which is attributed to the high degree of crystallinity of this polyester family. Finally, the poly(3-hydroxybutyrate) barrier properties against CO<sub>2</sub> are successfully compared with those of some selected common thermoplastics. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2391–2399, 1999

**Key words:** poly(3-hydroxybutyrate); poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); carbon dioxide; transport properties

# **INTRODUCTION**

Poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [P(HB-HV)] copolymers comprise a family of thermoplastic polyesters produced by many bacteria using renewable feedstocks, such as glucose and propionic acid.<sup>1–3</sup> Owing to their natural origin, these polymers are biocompatible and biodegradable by bac-

teria, fungi, and algae. In particular, they are clearly biodegraded in domestic sewage treatment systems, including aerobic and anaerobic processes, in sea water sediments, and in wet soils. But the distinct feature of these polyhydroxyalkanoates is that their biodegradation rate in moist air is negligible, so that their shelf-life should be long enough for most end uses.<sup>4</sup>

The picture emerging from this ensemble of characteristics is that of an environmentally friendly plastic material with potential applications in several fields.<sup>4</sup> Packaging is one of them, provided that both mechanical and transport properties are adequate. It has already been stated that P(HB-HV) copolymers offer a range of

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physical properties from the relatively stiff PHB and low 3-hydroxyvalerate (3HV) copolymers to the more flexible and tougher high 3HV grades. The former are suitable for general injection molding applications, such as bottle caps, whereas the latter can be made into sheets or blown films. High 3HV copolymers have been successfully used to make shampoo bottles with good performance.<sup>5,6</sup>

Few data have been published about the gas transport properties of these materials,<sup>7</sup> although it has been pointed out that P(HB-HV) copolymers offer interesting general barrier properties for water and gases.<sup>4,5</sup> This article is part of a project aimed at the characterization of PHB and P(HB-HV) transport properties.<sup>8-10</sup> In the following paragraphs, the transport of CO<sub>2</sub>, a subject of great importance in the field of packaging, will be studied in these materials by means of a gravimetric technique, as well as a pressure decay apparatus.

#### **EXPERIMENTAL**

#### Materials

The polymers used in this study were the PHB homopolymer and three copolymers, with nominal contents in 3HV repeating units of 8, 14, and 24%, all of them purchased from Aldrich. In the following sections, these copolymers will be referred to as PBV8, PBV14, and PBV24.

Films of uniform thickness around 35  $\mu$ m were solvent cast from 3% chloroform solutions over a smooth polytetrafluoroethylene surface. After slow evaporation of the solvent, the films received a thermal treatment of 3 weeks at 60°C to ensure full solvent removal and complete crystallization.

#### **Methods**

Thermal analysis was conducted on a Perkin– Elmer DSC-2C differential scanning calorimeter, using indium and dodecane as calibration references. Film samples of ~ 10 mg were encapsulated in aluminum pans and heated from -40 to  $190^{\circ}$ C at  $20^{\circ}$  min<sup>-1</sup>. From this first scan, melting enthalpies and temperatures were determined. After 1 min at this temperature, the samples were rapidly cooled to  $-40^{\circ}$ C and, from a second scan in identical conditions, the glass transitions were measured. Densities were measured in an aqueous NaBr density gradient column and calibrated with glass balls having a precision of 0.0001 g cm<sup>-3</sup>. Film thicknesses, measured with a Duo-Check ST-10 gauge having a precision of 1  $\mu$ m, were taken as an average of at least 30 individual measurements in each film sample.

 $\rm CO_2$  transport properties were measured using a Cahn D-200 electrobalance enclosed in a chamber thermostated at the desired temperature. Prior to each measurement, the polymer samples (~ 100 mg), were degassed in the electrobalance under a vacuum of  $10^{-2}$  torr, until a constant weight was achieved. Then, gas at the selected pressure (up to 1 atm) was introduced in the balance, and the weight change of the sample was recorded until equilibrium was reached.<sup>8</sup>

 $\text{CO}_2$  solubility was calculated from the equilibrium weight gain  $(M_{\infty})$  of the membrane after correction for buoyancy, by means of the relation:

$$C_o\left(\frac{\mathrm{cm}^3 \mathrm{STP}}{\mathrm{cm}^3}\right) = \frac{22414 \cdot M_{\infty}}{44 \cdot V_{plm}} \tag{1}$$

where  $V_{plm}$  is the volume of the polymer sample in cm<sup>3</sup>,  $M_{\infty}$  is in g, and 44 is the CO<sub>2</sub> molecular weight. Because the solubility isotherms were linear, Henry's Law solubility coefficients ( $K_H$ ) were calculated from the slopes of the sorption against pressure plots<sup>11,12</sup>:

$$C_o = K_H \cdot p \tag{2}$$

with  $K_H$  in (cm<sup>3</sup> STP cm<sup>-3</sup> cm<sup>-1</sup> Hg<sup>-1</sup>), and p, the applied CO<sub>2</sub> pressure, in cm Hg. Diffusion coefficients  $[D(\text{cm}^2 \text{ s}^{-1})]$  were calculated from the long-term solution of Fick's diffusion equation using the expression<sup>13</sup>:

$$\ln\left(1 - \frac{M_t}{M_{\infty}}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D \cdot \pi^2}{\ell^2} \cdot t$$
 (3)

A plot of  $\ln(1 - M_t/M_{\infty})$  versus time should give a straight line with a slope of  $D\pi^2/\ell^2$  (here,  $\ell$ is the film thickness). This equation assumes that D is independent of the penetrant concentration. However, its use was justified since our previous experience with the PHB/CO<sub>2</sub> system indicated that D was constant at least in the range of subatmospheric pressures.<sup>8</sup>

Two sets of experiments were performed in the Cahn electrobalance. First, gas sorption was investigated at 35°C and at 200, 400, 600, 800 and

950 mbar for the polymers of interest. Second, a series of sorption studies were performed in the same films at temperatures ranging from 25° to 50°C in 5° steps, with a pressure of 950 mbar, to investigate the temperature influence on the sorption process. Samples were stored in a desiccator during the period of time between both series of experiments ( $\sim 2$  months for all films).

An additional set of 35°C  $CO_2$  sorption measurements was made in a pressure decay sorption cell. A single transducer, dual volume-type apparatus was used, with a range of measurement from 0 to 30 atm. The design and operation of this system have been described elsewhere.<sup>14,15</sup> This technique was used to study the  $CO_2$  sorption behavior at pressures higher than those achievable in the Cahn electrobalance (up to 1 atm), as well as to establish comparisons between the results obtained with both techniques.

# **RESULTS AND DISCUSSION**

### **Sample Characterization**

P(HB-HV) copolymers display the unusual feature of reaching approximately the same high level of crystallinity at all compositions<sup>16-18</sup> (up to 70%). This is due to their ability to display isodimorphism: 3HV units are able to crystallize in the PHB lattice at compositions up to 40% 3HV mol content, and vice-versa at higher percentages. However, the 3HV units tend to act as defects in the PHB crystalline structure, in such a manner that they are partially excluded from the crystals. The degree of exclusion is dependent on the conditions of crystallization; however, it has been estimated that the 3HV concentration in the crystalline phase tends to be in the order of twothirds of the overall concentration in the copolymer.<sup>19,20</sup> This variable degree of exclusion makes difficult the calculation of a fully confident value for the melting enthalpy of the 100% crystalline material ( $\Delta H_m^0$ ). A relationship that has been proposed to relate  $\Delta H_m^0$  with the comonomer content of the copolymer is<sup>19</sup>:

 $\Delta H_m^0 (\text{J g}^{-1}) = 132 - 2.642 \cdot (2/3 \cdot X_V)$ 

with  $X_V$  being the 3HV percentage in the copolymer. This expression can be used to give a tentative estimation of the copolymer degrees of crystallinity from the melting enthalpies ( $\Delta H_m$ ), ob-



**Figure 1** DSC heating curves of typical PHB and P(HB-HV) films prepared as described in the text.

tained from the differential scanning calorimetry (DSC) measurements.

The features described herein are traduced in a complex crystalline phase, as it is revealed by the shape of the melting endotherms shown in Figure 1. The broad range of melting temperatures is indicative of the existence of crystals of varied qualities, especially in the case of the copolymers, where unstable, low temperature crystals are predominant. When multiple melting peaks appear in the thermograms, it is customary to consider the lower temperature peak as representative of the crystals originally present in the material.<sup>21–24</sup> It has been shown that the upper melting peaks are caused by melting and recrystallization of the most unstable crystals during the DSC scan.<sup>21–24</sup> All the thermal parameters of the samples used, together with density data, are summarized in Table I.

#### **Sorption Experiments**

 $\rm CO_2$  sorption isotherms at 35°C in PHB and the three selected copolymers appear in Figure 2 (subatmospheric pressures) and Figure 3 (high pressures). As can be seen in the figures, all the isotherms are linear over the range of pressures studied. This behavior was expected, because the polymers are above  $T_g$ .<sup>25</sup> The values of the Henry's law sorption coefficients obtained from the slopes of both sets of experiments are presented in Figure 4. In this figure, the error bars indicate the standard deviation of the individual  $K_H$  values calculated by applying  $K_H = C_0/p$  to each low pressure sorption result (the standard deviation of the high-pressure data, calculated in a similar

	Density (g cm <sup>-3</sup> )	$T_{g}$ (°C)	$\begin{array}{c}T_{m}^{1}\\(^{\circ}\mathrm{C})\end{array}$	$T_m^2$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	Crystallinity (%)
PHB	1.242	1	160	173	101	77
PBV8	1.231	2	146	157	78	67
PBV14	1.217	-2	139	151	72	67
PBV24	1.211	- 3	96	125	68	75

Table I Characterization of the Films Used in the CO<sub>2</sub> Sorption Experiments

*Note:*  $T_m^1$  and  $T_m^2$  are the temperatures of the two highest melting peaks present in the DSC thermograms.

fashion, were equal or smaller; not shown for clarity). Sorption coefficients obtained from both techniques are gratifyingly coincident in general terms, especially if the different nature of the experimental techniques is considered. Differences observed can be attributable to small differ-



**Figure 2** Low-pressure  $CO_2$  sorption in PHB and P(HB-HV) at 35°C.



Figure 3 High-pressure  $CO_2$  sorption in PHB and P(HB-HV) at 35°C.

ences in the actual degree of crystallinity of the particular samples of each polymer used. In the worst case, that of PBV24, we have estimated that the 7% discrepancy in the sorption results could be justified by a difference in the crystallinity of the samples of  $\sim 1.5\%$ . This is smaller than the uncertainty in the enthalpy of fusion, as measured by DSC, which is usually considered to be at least 2% of the value.

The 35°C diffusion coefficients, obtained as averages of the results at the various subatmospheric pressures studied, are presented in Figure 5 against the 3HV content of the copolymer. They also included the standard deviations from the respective averages. In the same figure, the permeability values were drawn, calculated as  $P = K_H \cdot D$ . Because, in this pressure range, the diffusion coefficients are constant and the sorption isotherms are linear, the estimation of P as the product of the diffusion and Henry's Law coefficients is justified.<sup>11</sup> As can be seen from Figures 4 and 5, the overall tendency of all the CO<sub>2</sub> transport parameters studied is to increase with the 3HV content, decaying for the 24% copolymer,



**Figure 4** Henry's Law sorption coefficients for  $CO_2$  at 35°C *versus* comonomer content in the copolymer.



**Figure 5**  $CO_2$  diffusion coefficients and calculated permeabilities at 35°C *versus* comonomer content in the copolymer.

which tends to have values of  $K_H$ , D, and P similar to those of PBV8. This behavior might be at least partly explained in terms of the different levels of crystallinity reached by each copolymer, following the trend displayed in Table I. All the sorption, diffusion, and permeability coefficients are summarized in Table II.

 $\rm CO_2$  sorption results at several temperatures from 25° to 50°C and 1 atm are shown in Figure 6, plotted as  $K_H$  versus the 3HV comonomer content. Using the Arrhenius equation,<sup>13</sup>

$$\ln(K_H) = \ln(K_H^0) - \frac{\Delta H_s}{RT}$$
(4)

the enthalpy of sorption  $(\Delta H_s)$  can be calculated from the slope of a  $\ln(K_H)$  versus 1/T plot. Because these plots are linear (see Fig. 7), it can be concluded that the sorption enthalpy is constant over the temperature interval considered. The re-



**Figure 6** Temperature dependence of Henry's Law  $CO_2$  sorption coefficient at 1 atm.

sults for  $\Delta H_s$  and  $\ln(K_H^0)$ , plotted in Figure 8, appear to follow the same qualitative dependence with the copolymer composition described in the preceding paragraph.

A careful comparison between the data presented in Figures 4 and 6 reveals some small differences. In particular, the 35°C sorption coefficients from Figure 6 have slightly increased, with respect to those presented before ( $\sim 15\%$  of the original value). As previously described, the same films were used in both series of experiments, with an interval of time in between. A certain conditioning effect could have taken place during storage, probably induced by the presence of residual CO<sub>2</sub> in the samples.

To verify the existence of this conditioning effect, we performed, with a fresh PBV14 sample, a set of measurements at various temperatures immediately after the first series at 35°C. In this case, no increase in the sorption levels was detected. These results, together with those ob-

 Table II
 CO2
 Transport Parameters in Poly(hydroxyalkanoates) at 35°C

	$(\mathrm{cm}^3 \mathrm{STP} \mathrm{cm})$	$H_{-3}^{H}$ cm Hg <sup>-1</sup> )			
	Low Pressure	High Pressure	$D \ (\mathrm{cm}^2 \ \mathrm{s}^{-1})$	P (Barrer) <sup>a</sup>	
PHB	0.0085	0.0082	$1.4 imes10^{-9}$	0.12	
PBV8	0.0097	0.0097	$2.2 imes10^{-9}$	0.21	
PBV14 DBV94	0.0104	0.0105	$3.2 \times 10^{-9}$ 2.6 × 10^{-9}	0.34	
1 D V 24	0.0100	0.0107	$2.0 \times 10$	0.20	

<sup>a</sup> 1 Barrer =  $10^{-10}$  cm<sup>3</sup> STP cm cm<sup>-2</sup> s<sup>-1</sup> cm<sup>-1</sup> Hg<sup>-1</sup>.



**Figure 7** Arrhenius plots of Henry's Law  $CO_2$  sorption coefficients.

tained 2 months later, are shown in Figure 9 for comparison. It demonstrates that the increase in sorptive capacity takes place only after storage of those films that have previously been exposed to  $CO_2$ . Accordingly, the sorption enthalpy slightly changes from -16.0 to -12.8 kJ mol<sup>-1</sup>.

Penetrant sorption-induced conditioning is commonplace in case of glassy polymers such as poly(ethylene terephtalate) (PET).<sup>25</sup> After exposure at high penetrant concentrations, the higher sorption capacity obtained is explained in terms of an increased free volume in the polymer. This excess of free volume remains after the penetrant has been withdrawn due to the nonequilibrium nature of the glassy state. In the case of the rubbery polyhydroxyalkanoates, this situation can be understood by taking into account the complexity of their crystalline morphology. It can be reason-



**Figure 8** Sorption enthalpies and preexponential factors in the  $25^{\circ}$ - $50^{\circ}$ C temperature range.



**Figure 9** Comparison between sorption data at several temperatures for a conditioned and unconditioned sample of PBV14.

ably argued that, having a high degree of crystallinity and a wide variety of crystal qualities, certain amorphous areas can become "hidden" to the penetrant molecules due to the presence of constrained tie molecules that obstruct their passage between the crystalline structures. Under this point of view, the remaining  $CO_2$  molecules in the exposed films might act as plasticizers, eventually inducing a partial relaxation of the constrained amorphous chains. Thus, the sorptive capacity would be increased because now more amorphous material is available for new  $CO_2$  molecules.

In Figure 10, PHB diffusion coefficients and the calculated permeabilities are plotted against temperature. Given that the mass uptake *versus* time plots of the copolymers became increasingly



Figure 10 Temperature dependence of experimental  $CO_2$  diffusion coefficients and calculated permeabilities for PHB.



**Figure 11** Some  $CO_2$  uptake plots showing non-Fickian behavior. A Fickian PHB uptake plot is also shown for comparison. From top to bottom: PBV24 at 50°C, PBV14 at 45°C, PBV8 at 50°C, and PHB at 45°C. Pressure: 1 atm.

non-Fickian when experiments at high temperatures were performed, no reliable diffusion coefficients could be obtained for these polymers to study the temperature effect on the diffusional process. Some of these plots are presented in Figure 11 for reference. It seems that some structural changes occur in the copolymers during the sorption process, affecting the macroscopic mass uptake. However, these changes were not permanent, because the final CO<sub>2</sub> uptake was reproducible. It must be emphasized that this kind of anomaly never took place during the measurements with PHB, but only with the copolymers at temperatures above 35°C. Again, the complex amorphous-crystalline morphology of the P(HB-HV) copolymers, as revealed by the DSC measurements, might be responsible for these departures from the ideal Fickian behavior.

The 25°C sorption coefficients, gravimetrically obtained in this work, compare very well with those presented elsewhere<sup>7</sup> as the cocient between permeability and diffusivity coefficients, obtained by means of a permeation method. These authors assumed a sorption behavior of the Henry's Law type, which implies linear sorption isotherms described by a constant value of  $K_H$  [see eq. (2)]. The validity of this assumption has been demonstrated here for a wide pressure range. The PHB diffusion and permeability data at 25°C are also comparable with the results presented in the mentioned work for copolymers containing 5 and 12% 3HV units, although these are significantly smaller. However, the permeability and diffusivity data shown in that work for a 27% copolymer appear to be 10 times higher than what would be expected, considering the trend shown in Figure 5 of the present work. This discrepancy might be explained by means of a very low crystallinity degree in this copolymer; however, it does not seem to be the case, because its sorption coefficient is consistent with our results for copolymers having crystallinities as high as  $\sim$  70%. The presence of pinholes in the samples used could be an alternative explanation for those apparent inconsistencies in the results for the 27% copolymer.

The PHB diffusional activation energy [calculated from a logarithmic expression equivalent to equation  $(4)^{13}$ ], together with all the sorption enthalpy values, are summarized in Table III.

## Evaluation of the P(HB-HV) CO<sub>2</sub> Transport Properties

The  $CO_2$  transport properties of some selected common polymers<sup>26,27</sup> are reviewed in Table IV, together with those of PHB obtained in this work. After consideration of the data presented in this table, the most remarkable conclusion that can be extracted about the PHB properties is its low permeability to  $CO_2$ . In fact, it is slightly lower than those of PVC and PET, polymers to which PHB has often been compared as regards to its barrier properties, having diffusion and solubility coefficients intermediate to them. When compared with data from the other polymers, it is also interesting to note that having a solubility coefficient relatively high, PHB diffusion coefficient is about 2 orders of magnitude smaller. This is also the case of PET; accordingly, it can be stated that the low  $CO_2$  diffusivity in these polyesters is the controlling factor in the permeation process. In the case of PHB, being a rubbery polymer with a flexible chain, this is mainly due to its high level of crystallinity, and the related tortuosity and

Table IIIThermodynamic Parametersfor the CO2Transport Processin Polyhydroxyalkanoates

	$\frac{\Delta H_s}{(\rm kJ\ mol^{-1})}$	$E_a$ (kJ mol <sup>-1</sup> )	$E_p = \Delta H_s + E_a$
PHB	-18.4	37.4	19.0
PBV8	-14.2	_	
PBV14	-12.8	_	
PBV24	-14.9		—

Material	Р	$D\cdot 10^9$	$K_H$	$E_p$	$E_{a}$	$\Delta H_s$
	0.005	0.74	0.0100	10.0	27 4	10 /
PHD	0.095	0.74	0.0129	19.0	37.4	-18.4
PVC <sup>a</sup>	0.160	2.5	0.0063	56.8	64.6	-7.8
$PET^{b}$	0.157	0.57	0.027	18.4	50.2	-31.4
Nylon 11 <sup>c</sup>	0.52	7.0	0.0074	33.9	51.9	-18.0
$EVA45^{27}$	92	430	0.021	31	41	-10
HDPE	0.36	120	0.0003	30.14	35.6	-5.5
Butyl rubber	5.2	57.8	0.0089	41.5	50.2	-8.7
Nitrocellulose	2.12	22.1	0.0096			

Table IV CO<sub>2</sub> Transport Properties of Several Common Polymers at 25°C and 1 atm<sup>26</sup>

<sup>a</sup> Unplasticized PVC.

<sup>b</sup> 40% crystalline.

<sup>c</sup> In dry conditions.

geometric impedance features imposed by the crystallites to the diffusing species.

As far as thermal parameters are concerned, the main feature of PHB is the low permeation energy of activation, which can be traduced in a low increment in permeability with the temperature. Therefore, its barrier character will be maintained in a range of temperatures, as it also happens for PET. These conclusions can be qualitatively extended to the activation energy of diffusion and the enthalpy of solution for the PHB/CO<sub>2</sub> system.

## **CONCLUSIONS**

 $\rm CO_2$  sorption experiments performed with PHB and various P(HB-HV) copolyesters show that these materials have good barrier properties. This is mainly due to the high degree of crystallinity in this family of biopolymers. The results obtained by combining a subatmospheric gravimetric method and a high pressure decay sorption cell indicate that the sorption behavior is linear at pressures up to 25 atm for all the copolymers studied. Excellent agreement between the results obtained by means of both techniques was demonstrated.

A certain susceptibility of these polymers with respect to  $CO_2$  has been evidenced. We have shown that exposure to  $CO_2$  can lead to slight increments in the sorptive capacity of polyhydroxyalkanoates. Non-Fickian behavior in the  $CO_2$  uptake at temperatures above 35°C was also evident, probably reflecting some kind of structural rearrangement induced by the penetrant. Both facts are clear evidences of the sensitivity of polyhydroxyalkanoates with respect to  $CO_2$ . Calculated permeabilities are comparable with those of PVC and PET. Accordingly, PHB and by extension P(HB-HV), can be included in the class of polymers offering good gas barrier properties against  $CO_2$ . This fact confirms the good balance of physicochemical properties that make this family of biopolymers a solid candidate for the development of a future biodegradable packaging material.

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