Evaluation of the transport properties of Poly(3-hydroxybutyrate) and its 3-hydroxyvalerate copolymers for packaging applications

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SUMMARY: Poly(3-hydroxybutyrate) (PHB) and ist 3-hydroxyvalerate containing copolymers form a family of fully biodegradable polyesters with many potential applications. In this work, the results obtained in our laboratory concerning carbon dioxide, water and organic solvent transport through PHB and three low 3-hydroxyvalerate copolymers are reviewed. Comparison established between the former results and some data taken from the literature, have revealed that PHB and the above mentioned copolymers show transport properties similar to other common thermoplastics such as PVC and PET, particularly in the case of carbon dioxide and water. Consequently, PHB and copolymers can be catalogued as good barrier materials against these penetrants. On the other hand, these biopolymers show a low barrier character against organic compound permeation. All these features conform a good balance of physicochemical properties for these polyhydroxyalkanoates, which may take them suitable for several applications, including its use in biodegradable packaging materials.

Introduction

PHB is fully biodegradable polyester produced by several kinds of bacteria. Although being rather brittle, PHB shows a combination of physical and processing properties similar to those of more conventional thermoplastics1). The development of its 3-hydroxyvalerate (3HV) containing copolymers [P(HB-HV)] has made available a new range of materials with better processability and improved physical properties, ranging from the stiff low 3HV content copolymers to the more flexible high 3HV grades2). Many practical applications taking advantage of the biodegradability of these polyhydroxyalkanoates (PHAs) have been suggested, including their use in medicine, agriculture and packaging films. However, little information has been published concerning their transport properties3), which is a subject of importance in assessing the usefulness of a polymer in packaging applications among others.

The objective of this work is to establish a first approach concerning the measurement of the PHB and P(HB-HV) transport properties, as well as their comparison with already published data for some commodity thermoplastics. The penetrants studied include carbon dioxide, water and several common solvents. Carbon dioxide is one of the most important gases in the food

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packaging field, together with nitrogen and oxygen. Apart from its role in the respiratory processes of packaged fresh vegetables and its bacteriostatic properties, the knowledge of the CO2 transport properties will serve to give a preliminary view of the general gas transport properties in PHB and its copolymers. Water is also a penetrant of importance for the packaging field, but also in other areas such as medicine, and even in general molding applications. In these cases, the amount of water that can be taken up by the polymer is of great interest. Finally, some organic compounds of varied nature will be used to measure the solvent permeation resistance of the title biopolymers.

Experimental

The samples used were PHB homopolymer, and three copolymers containing 8, 14 and 24% 3-hydroxyvalerate units, which will be referred to as PBV8, PBV14 and PBV24 in this work. All the polymers used were purchased from Aldrich. Thin films of constant thickness between 25 and 50 microns were obtained after casting from chloroform solutions. After a thermal treatment at 60°C to eliminate solvent residues and ensure complete crystallization, the average crystallinity of the samples used was around 70%, as determined by DSC4).

Water5) and carbon dioxide sorption4) was determined gravimetrically by using a thermostated Cahn D-200 electromicrobalance. Water sorption was measured at activities from 0.03 to 0.94, while carbon dioxide was investigated at pressures up to 1 atm. From the initial transient stage of the sorption process, the corresponding diffusion coefficients were determined according to well established methods6). The carbon dioxide permeability coefficients were calculated from the product of the solubility and diffusion coefficients. A series of high pressure sorption measurements was performed in a pressure decay sorption cell. Thus, carbon dioxide solubility was also investigated at pressures up to 25 atm.

Water and organic vapour permeability were determined by means of a gravimetric permeation cell7). Diffusion coefficients for the solvents studied (methyl ethyl ketone, n-butyl acetate, toluene, methanol and carbon tetrachloride, among others) were obtained by the well known time lag method6).

Transport properties of PHB and P(HB-HV) copolymers

1. Carbon dioxide

The carbon dioxide sorption isotherms in PHB and P(HB-HV) copolymers at 35°C were linear over all the range of pressures studied, both at subatmospheric and high pressures up to 25 atm. Accordingly, the solubility coefficient (K_H), obtained after Henry's Law from[6)]

$$K_H\,(\text{cm}^3\text{STP/cm}^3\ \text{cmHg}) = C(\text{cm}^3\text{STP/cm}^3)\ /\ p(\text{cmHg}) \qquad (1)$$

(C being the amount of gas sorbed, and p the gas pressure) is not dependent on the penetrant concentration in the polymer, which is the typical behaviour exhibited by rubbery polymers, as it is the present case. Since the diffusion coefficients (D) measured were also independent on the penetrant concentration, the permeability coefficient can be adequately estimated from the product of these magnitudes[6)], expressed in the appropriate units as

$$P(\text{Barrer}) = 10^{10}\ KH\,(\text{cm}^3\text{STP/cm}^3\ \text{cm Hg}) \times D\,(\text{cm}^2/\text{s}) \qquad (2)$$

(1 Barrer = 10^{-10} cm^3STP cm/cm^3 cm Hg s). All these parameters are summarized in Tab. 1.

Table 1: Carbon dioxide transport parameters at 35°C

polymer	K_H	D	P
PHB	0.0085	1.4 10-9	0.12
PBV8	0.0097	2.2 10-9	0.21
PBV14	0.0104	3.2 10-9	0.34
PBV24	0.0100	2.6 10-9	0.26

As can be observed, the overall tendency of all these transport parameters is to increase with the 3HV content up to a 14%, decaying for the 24% copolymer, which tends to have values of K_H, D and P similar to those of PBV8. This trend may be reasonably explained in terms of small differences in the levels of crystallinity reached by each copolymer, rather than structural or chemical differences between these copolymers.

2. Water

In a typical sorption experiment, the amount of mass gained by the polymer after exposure to a set pressure of the penetrant increases progressively until an equilibrium is reached, which is characterized by a constant weight of the sample. This is the behaviour initially observed during the sorption experiments performed with carbon dioxide and water as penetrants. However, in the case of water, if more weight data are recorded after equilibrium is apparently reached, a decrease in the mass sorbed by the polymer is observed until a new equilibrium is reached, after an induction period that depends on the water vapor pressure and the sample thickness[5]. This effect significatively modifies the water solubility at high water activities (above 0.7), with weight losses of about 30% with respect to the maximum uptake. The most probable cause for this behaviour is probably macromolecular relaxations following the initial entrance of water molecules in the polymer. In Fig. 1 the sorption data corresponding to the first apparent equilibrium, together with the true equilibrium data, are plotted for the case of PHB at 40°C. It should be taken into consideration that the pseudoequilibrium data define an upper limit in the water sorption capacity of the polymer, that can be of even more technological interest than the lower equilibrium solubilities. Experiments performed with the copolymers indicate a similar performance in the sorption of water vapor, with no significative differences between them (data not shown). Fig. 2 summarizes the water diffusion coefficients in PHB and PBV14 films.

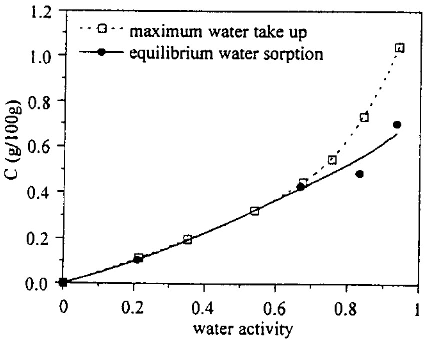

Fig. 1: Water sorption in PHB films at 40°C

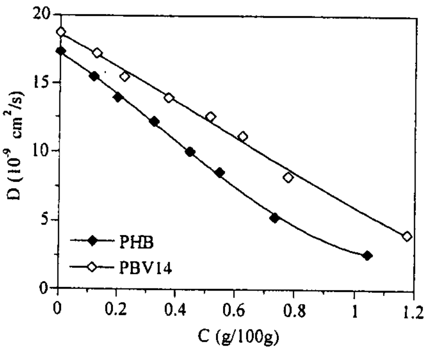

Fig. 2: Water diffusion coefficients in PHB and PBV14

As can be observed, the diffusion coefficients show a monotonous decrease with the water concentration in the polymer. This behaviour, togethe with the sharp upturn in the sorption curve of Fig. 1 (dotted line), is usually interpreted as a clear indication that the water molecules sorbed in the polymer tend to aggregate between them to form clusters. This effect is due to the predominance of water-water versus water-polymer interactions, in particular H bond formation between neighbouring water molecules. The clustering analysis of Zimm and Lundberg[8)] provides mathematical expressions to quantify the average number of water molecules per cluster formed. The results of this analysis for PHB and PBV14 sorption experiments are shown in Fig. 3, where a clear tendency of the sorbed water to form clusters of increasing size is evidenced, especially at water activities above 0.6.

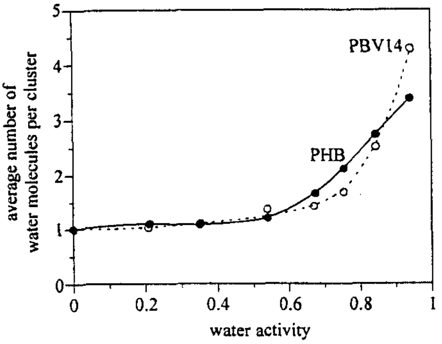

Fig. 3: Water clustering in PHB and PBV14′

The water vapor transmission rates (WVTR, in g mm/mm^2 day units) obtained from permeation experiments, as the average of triplicate measurements to ensure reproducibility, are presented in Table 2. These results seem to indicate that as in the case of sorption, the permeability is again essentially independent of the 3HV content of the copolymer.

Table 2: Water vapor transmission rates through PHB and P(HB-HV) copolymers at 30°C. (Relative humidity difference across the membrane: 100-33%)

3% HV	WVTR (g mm/m^2 day)	standard deviation
0	1.16	0.08
8	0.92	0.03
14	1.39	0.19
24	1.22	0.12

3. Organic vapors

The vapor transmission rates (VTR, in g mm/m^2 day) of several organic chemicals commonly used as solvents in the industry has been measured in PHB, PBV14 and PBV24 films under conditions of 100% pure vapor in the feed side of the membrane, being effectively zero the penetrant partial pressure at the downstream side$^{9)}$. Prior to study the variation of the vapor transmission rates with the comonomer content of the copolymer, it is interesting to first consider how the transport properties change with the structure of the penetrant for the homopolymer of reference$^{7)}$.

In Table 3 the permeabilities in Barrers of several solvents through PHB are presented.

Table 3: Organic vapor permeability through PHB films at 30°C

Penetrant	P(Barrer)
acetone	2830
n-butyl acetate	2340
toluene	2020
methanol	914
water	864
carbon tetrachkoride	314
n-hexane	108
isopropyl ether	25

The use of the permeability coefficient expressed in Barrers is particularly interesting, since these units are normalized to the vapor pressure exerted by the penetrant (in cmHg). From this table, it can be seen that the highest permeabilities correspond to molecules with moderately polar structures such as acetone, butyl acetate and toluene, which have a level of polarity roughly similar to the polymer investigated, PHB. Chemicals having structures of very high polarity (methanol and water, also included here for comparison) or completely apolar (the last three molecules included in Table 3 show the lowest permeabilities due to a low level of interaction with the polymer.

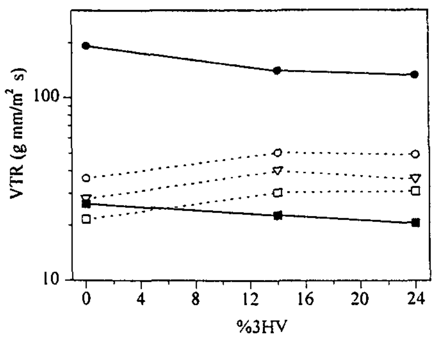

Fig. 4: Vapor transmission rates as a function of the 3HV content in the copolymer.
Symbols: ● , MEK; o, toluene; ∇ , CCl4; □, methanol; ■, n-butyl acetate

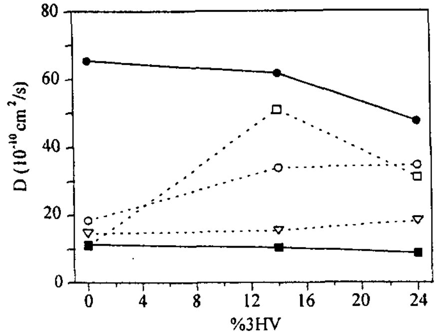

Fig. 5: Diffusion coefficients as a function of the 3HV content in the copolymer.
Same symbols than in Fig. 4

The variation of the vapor transmission rate and the diffusion coefficients with the comonomer content of the copolymer is shown in Figs. 5 and 5. Interestingly, the molecules containing a carbonyl group in their structure (methyl ether ketone,MEK, and n-butyl acetate), a functional group that is also present in the polymeric chains, present VTR values which tend to decrease with the 3HV content. By contrast, the other compounds included in this figure tend to have increasing VTR values. It is quite difficult to find a reasonable explanation for this behaviour, since there are several factors involved in the permeation process, such as the molecular size and shape of the penetrants, the existence of different penetrant-polymer degrees of interaction, and the complexity of the amorphous-crystalline morphologies developed in each copolymer. The variation of the diffusion coefficient is even more complex, as can be seen in Fig. 5, although the trend described above is still followed.

Evaluation of the PHB and P(HB-HV) transport properties by comparison with literature data

1. Carbon dioxide

The PHB, PBV8 and PBV14 carbon dioxide sorption isotherms are compared in Fig. 6 with that of PET, in the pressure range of 3-15 atm. The PET isotherm shows the typical concave shape commonly found in glassy polymers, according to the well-known Dual Mode of sorption10). Thus, the overall PET sorption isotherm is the sum of two contributions: the dissolution of the gas in the polymer matrix (which is the mechanism operating in the case of PHB and copolymers, giving linear isotherms according to Henry's law), and the superficial Langmuir adsorption into the microcavities existing in glassy polymers.

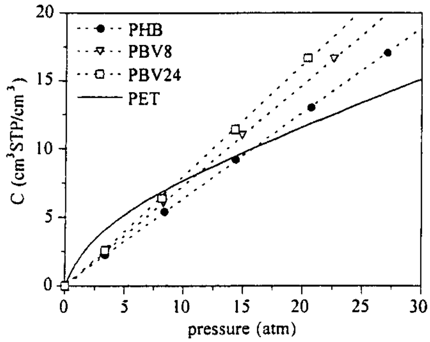

Fig. 6: High pressure CO_2 sorption comparative (35°C)

As can be seen in this figure, the general sorption levels are quite similar for PET and PHAs. In particular, PHAs perform better around 4 atm, which is the typical carbon dioxide pressure applied in containers for carbonated beverages. This point is of interests since, as it was shown as early as 25 years ago, the main cause for pressure losses during the first stages of storage in PET bottles was due to the gas sorption in the plastic walls11). More specifically, it was calculated that a reduction from 100 to 30 days in the storage time required for a 10% pressure loss in the bottles, was due to the above mentioned Langmuir adsorption in microcavities, a contribution that is not present in the case of PHAs.

The CO_2 permeability of several common polymeric materials at 25°C are summarized in Table 4. As can be seen in this table, PHB shows a permeability value very close to PET and unplasticized PVC, which are usually considered as being relatively low permeable to CO_2. Accordingly PHB, and by extension P(HB-HV) copolymers, can be considered as good barriers against carbon dioxide permeation.

Table 4: CO_2 permeabilities and water vapor transmission rates for various polymers[12)]

polymer	$P(CO_2)^a$	$WVTR^b$
Saran	0.04	0.11
Nylon 6	0.05^c	7.5^c
PHB	0.09	1.16
PET	0.10	0.71
uPVC	0.12	1.18
cellophane[13)]	0.002^c	140^c
PP	3.2	0.59
PS	8.0	4.0

[a] at 25°C, 0%RH (except Nylon 6, 80%RH)

[b] at 40°C, 90%RH (except PHB, 30°C)

[c] performance strongly dependent on % RH

2. Water vapor

Water vapor transmission rates are included in Table 4, together with the carbon dioxide permeability values. Again, the PHB value is very similar to that of PET and PVC, so that the same conclusions about a good barrier character of PHB can be extracted for comparison with these polymers. As far as water is concerned, PHAs present the advantage of their hydrophobicity when compared to other biopolymers of natural origin, such as starch. In this case, the high hydrophilic character of this polymer is traduced in a WVTR value of 1030 g mm/m^2 day (measured at 38°C and 100-30% RH)[14)], as well as its associated water sensitivity.

From Fig. 8 can be seen that the PHB vapor transmission rates are two orders of magnitude higher than those of PET, independently of the chemical nature of the solvent considered. In this case, PHB is in general terms comparable to LDPE, having lower permeabilities for apolar molecules such as n-hexane, and higher values for polar ones (acetone, methanol).

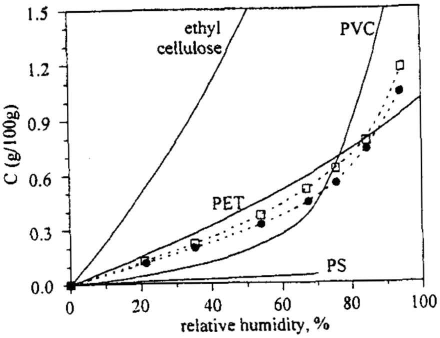

Fig. 7: Water sorption comparative[15,16]
Symbols: ●, PHB; □, PBV14.

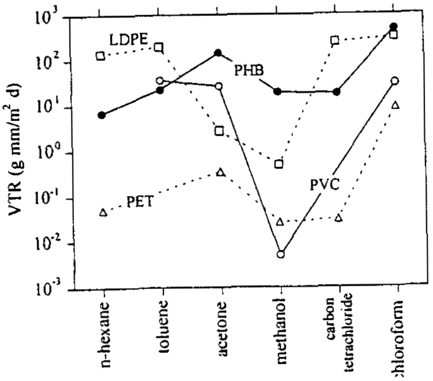

Fig. 8: Compared permeation rates of PHB, LDPE[17], PVC[18] and PET[12,18] (23°C)

The reasons for the high permeability of PHAs to organic solvents are probably related to the high mobility of their polymeric chains, as their low glass transition temperatures indicate (around 0°C for the copolymers studied in this work)[14]. Thus, even molecules having very low affinity for the polyester chains, such as n-hexane or the bulky carbon tetrachloride, have the ability to move across the polymeric media with enough ease to be traduced in a relatively high vapor transmission. This interpretation is also applicable to LDPE; however, it is worth noting that the low barrier offered by LDPE against organics has not prevented this polymer from becoming a widespread polymer in the packaging field. This is due to the fact that in few applications is a high resistance against the permeation of pure organic vapors specifically required.

Conclusions

After all the above considerations, PHB and P(HB-HV) copolymers can be classified in general terms as good barrier polymers, having gas and water transport properties similar to commodity thermoplastics such as PVC and PET. Since it is usually considered that carbon dioxide permeation rates are three to four times that of oxygen in almost all polymers¹³⁾, a rough estimation can be made using the CO_2 permeability values obtained in this work This gives a value around 0.03 Barrers at 25°C for PHB; consequently, PHB can also be considered a good barrier for oxygen.

Taking advantage of this combination of conventional thermoplastic properties, as well as their truly biodegradability and biosynthetic origin, PHAs conform one of the leading families of biodegradable polymers which can potentially substitute conventional petroleum-based plastics in several applications.

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