# Immobilization Influence on the Water Sorption and Diffusion in Poly(3-hydroxybutyrate)

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ABSTRACT: The temperature dependency of water vapor sorption and diffusion in poly(3-hydroxybutyrate) (PHB) was studied for the first time. Equilibrium sorption and diffusion kinetics were determined by a quartz McBain's vacuum microbalance technique in the temperature range of 303–333 K. A probability of water molecule interaction with the polymer matrix was analyzed for wet PHB films by FTIR spectroscopy technique. Sorption isotherms are interpreted as the solution of free water molecules estimated by the Flory–Huggins equation and the sorption of water molecules immobilized on the carbonyl groups of PHB. The immobilization effect was described by a Langmuir-type equation. The dependency of diffusivity on water concentration was described in the frames of Fujita's immobilization model in which the growing function  $D_w$  versus  $C_w$  characterized the filling degree of carbonyl groups as sites of immobilization (42 kJ/mol), as well as the activation energy of water diffusion coefficients (71 kJ/mol), in noncrystalline areas of PHB were determined. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 981–985, 1999

Key words: immobilization; water sorption-diffusion; poly(3-hydroxybutyrate)

## INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a representative of the class of poly(hydroxyalkanoates).<sup>1</sup> It is characterized by a fortunate combination of high technological effectiveness,<sup>2</sup> useful physicochemical characteristics (indexes),<sup>3,4</sup> adjustable ability to biodegradation,<sup>3,5</sup> and ecological compatibility with the environment.<sup>6,7</sup> Due to fair compatibility with biological media, this polymer is coming into use in medicine and veterinary science.<sup>8,9</sup>

PHB decomposes to carbon dioxide and water under natural conditions, under the effect of bacteria and enzymes. This makes it useful for agriculture and as an environmentally friendly, pure packing material.<sup>10</sup> At the same time, transport characteristics, which are the main factors determining chemical resistance and the areas of possible application of polymers, were not yet studied for PHB.

The objective of this work was to study sorption-diffusion indexes of the PHB-water system in a wide temperature range. Development in progress of the model of water sorption-diffusion in moderately hydrophobic polymers is of special interest. PHB is one of these polymers.

#### EXPERIMENTAL

PHB films of the Biomer Co. (City, Germany), cast from chloroform, were studied in the work.

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The thickness of the resulting films was  $80 \pm 5 \mu$ m, and the degree of crystallinity estimated by X-ray diffraction analysis was about 70%.<sup>12</sup> The starting polymer powder was partially dissolved in chloroform upon prolonged boiling. Its solubility was found to be about 0.01 g/mL. A hot solution was filtered through a glassy Shott's filter. The molecular mass of the filtered substance was determined by the viscosimetric technique by using the following equation:<sup>13</sup>

$$[\eta] = 7.7 \times 10^{-5} M_w^{0.82} \tag{1}$$

where  $[\eta]$  is the characteristic viscosity of the polymer solution in chloroform.

The viscosity-average molecular mass of the polymer  $M_w$  was found to be  $83.5 \times 10^3$  g/mol. On the basis of the data on polydispersities of PHB,<sup>13</sup> the number-average molecular mass  $M_n$  was found to be  $35.5 \times 10^3$  g/mol.

Tests on sorption were performed by vacuum gravimetry by using McBain's vacuum microbalance with 0.67 mg/mm sensitivity of quartz spring. Details of the equipment used in the sorption experiment are described in Ref. 14.

The IR spectra of PHB films were recorded with an FTIR Bruker IFS-48 spectrometer with a resolution of 2 cm<sup>-1</sup>. The scan number was 250-400. The data on the characteristic absorption bands were processed with Bruker software.

#### **RESULTS AND DISCUSSION**

Isotherms of water vapor sorption by PHB films obtained in the temperature range of 303–333 K are shown in Figure 1. The results shown were recalculated for the amorphous phase of the polymer. As seen from Figure 1, sorption isotherms show a specific convexity directed to the ordinate axis. As the relative pressure of water vapors  $p/p_0$  rises, each isotherm approaches a limiting value. The lower the temperature of the experiment, the more pronounced the limit.

To interpret sorption isotherms analogous to the double sorption model,<sup>15</sup> we have assumed the existence of immobilized (on polar groups, sorption centers) and free water (molecularly dissolved, possessing translational mobility) in the polymer. There exists a dynamic balance between these forms of water. The total concentration of water in the polymer can be presented as the sum of two constituents:



**Figure 1** Sorption isotherms for water vapors in PHB films at different temperatures. Subdivision of the sorption isotherm into two terms at 313 K is shown as an example. See the text for details.

$$C_w = C_{wf} + C_{wl} \tag{2}$$

where  $C_{wf}$  is the concentration of free (mobile) water and  $C_{wl}$  is the concentration of water immobilized in the polymer on the sorption centers. The first component is determined by Henry's law:

$$C_{wf} = K_H \alpha_w \tag{3}$$

where  $a_w$  is the activity of water, and  $K_H$  is the Henry's Law constant. According to the Langmuir model, the second constituent appears to be quite traditional for the dual-mode sorption model:

$$C_{wl} = \frac{C_H K C_{Wf}}{1 + K C_{Wf}} \tag{4}$$

Here  $C_H$  is the concentration of the accessible sorption centers, and K is the equilibrium constant of the Langmuir sorption.

To estimate the content of free water in PHB, we used the Flory–Huggins equation. When the content of water is small, this equation can be simplified<sup>16</sup> to

$$K_H = \exp(-(1+\chi)) \tag{5}$$

Table I Values of Henry $(K_H)$ and
Flory–Huggins ( $\chi$ ) Constants and Equilibrium
(K) and Effective Sorption Center
Concentration $(C_H)$ Constants for the
<b>PHB-Water System at Different Temperatures</b>

<i>T</i> , (K)	X	$\begin{array}{c} K_H \times \ 10^3 \\ ({\rm g/cm^3}) \end{array}$	$K imes 10^{-2}\ (\mathrm{cm}^{3}\mathrm{/g})$	$C_H  imes ~ 10^3 \ ({ m g/cm}^3)$
303	5.4	1.6	6.9	8.3
313	5.2	1.9	6.8	12
323	5.1	2.2	2.3	27
333	4.9	2.6	1.8	34

where  $\chi$  is the Flory–Huggins constant, determined by the group contribution method calculating the solubility parameter of PHB  $\delta_{\text{PHB}}^{11,17}$  and  $\chi$  for various temperatures:

$$\chi = \frac{V_1(H_2O)(\delta_{\rm H_2O} - \delta_{\rm PHB})^2}{RT}$$
(6)

Here  $V_1(H_2O)$  is the partial molar volume of water molecules,  $\delta_{H_2O}$  is the solubility parameter of water, *T* is the absolute temperature, and *R* is the universal gas constant.

If we separate the experimental isotherms into constituents corresponding to free and bound water, we get the rest parameters of eq. (4). The relevant data for various temperatures are presented in Table I.

An example of experimental isotherm subdivision into two modes is shown in Figure 1, which shows that the concentration of free water in polymer  $(C_{Wf})$  is significantly lower than the concentration of water, linked to the sorption centers:  $C_W \approx C_{wl}$ .

To explain the diffusional experiments we suggested that the mobility of water molecules, linked to the sorption centers of the polymer, can be ignored. Therefore, the efficient flow of water molecules diffusing in PHB, observed experimentally, is developed only by the migration of free water molecules in the polymer.

In the framework of this model, the relationship for effective diffusion coefficients  $(D_{\rm eff})$  is the following:  $^{14}$ 

$$D_{\rm eff} = D_{Wf} \frac{\partial C_{Wf}}{\partial C_W} \tag{7}$$

Here  $D_{Wf}$  is the diffusion coefficient of water in the absence of sorption centers in the polymer matrix.

Taking into account that free water concentration  $(C_{wf})$  is markedly smaller than the concentration of water immobilized on the sorption centers and using eq. (4), we obtain the dependency of  $C_{wf}$  versus  $C_w$  that is analogous to the classic relationship:<sup>14</sup>

$$C_{Wf} = \frac{\alpha C_W}{1 - \beta C_W} \tag{8}$$

where  $\alpha$  and  $\beta$  are constants:

$$\alpha = \frac{1}{KC_H}, \quad \beta = \frac{1}{C_H} \tag{9}$$

If eqs. (7) and (8) are solved jointly, we get an equation relating the effective diffusivity to the concentration of sorbed water in the polymer:

$$D_{\rm eff} = \frac{\alpha D_{Wf}}{(1 - \beta C_W)^2} \tag{10}$$

An equation similar to eq. (10) was first deduced by Fujita.<sup>18</sup>

Figure 2 shows the concentration dependencies of diffusion coefficients for various temperatures. In accordance with Fujita's diffusional model, the concentrational dependency of experimental (effective) diffusion coefficients  $D_{\rm eff}$  can be linearized in the  $(D_{\rm eff})^2 - C_w$  coordinates. This is the case within the temperature interval studied.



**Figure 2** Concentrational dependencies of water diffusion coefficients in PHB at different temperatures in the coordinates of eq. (10). Dotted lines mark calculated values, points mark the experimental data.

<i>T</i> , (K)	$D_{Wf}  imes 10^8 \ ({ m cm}^2/{ m s})$	$D_{W\mathrm{eff}(C ightarrow 0)}  imes 10^8 \ (\mathrm{cm}^2\!/\mathrm{s})$
303	1.6	2.3
313	4.5	10
323	18	33
333	28	37

Table IIWater Diffusion Coefficients in PHBat Different Temperatures

Treatment of the experimental data in these coordinates by the regression analysis method gave the diffusivities of free water (i.e. water molecules that migrate in the polymer matrix in the absence of sorption centers). Note that in eq. (10) we used the values of the diffusion constants  $\alpha$  and  $\beta$  obtained from the equilibrium sorption data, that is, from the independent experiment. The values of  $D_{Wf}$  are shown in Table II.

Low values of effective diffusion coefficients compared with those of free water support the existence of interaction between diffusing molecules and polymer matrix. Probably, such interaction is mainly determined by the presence of carbonyl groups in PHB that are capable of hydrogen bonding with water molecules. Previous results<sup>19</sup> demonstrate the possibility that such interactions would proceed with the formation of cyclic structures in polymers in the presence of water.

In the present case, we cannot say that any effect of cyclic structures of water diffusion exists. However, the presence of two types of carbonyl groups in PHB<sup>17,19</sup> is confirmed by recorded IR spectra, from which the second derivatives of absorption intensity in the range of 1749-1722 cm<sup>-1</sup> were built (see Fig. 3). Figure 3 shows the results of water interaction with carbonyl groups in PHB, and as a consequence, an increase of the peak intensity of carbonyl groups ( $1724 \text{ cm}^{-1}$ ) and an decrease of the peak intensity of free carbonyl groups ( $1747 \text{ cm}^{-1}$ ). This indicates that some free carbonyl groups become bound to water molecules.

The analysis of the temperature dependency of free water diffusion coefficients and effective diffusion coefficients, extrapolated to the zero sorbate concentration  $(D_{w \text{ eff}(C \rightarrow O)})$  (see Table II), shows that activation energies of diffusion are rather high (71–84 kJ/mol). Probably, these high values of activation energy suggest that there exists a barrier to the formation of the diffusion

activation volume in the highly crystalline matrix of PHB.

Analyzing temperature dependencies of the equilibrium sorption parameters from Table I, one may note that the solubility coefficient (the Henry constant) of free water increases with temperature. The heat of water dissolution in the PHB matrix is rather small and is equal to 12 kJ/mol. The small heat effect of sorption is also typical of moderately hydrophobic polymers.<sup>20</sup> Note that the enthalpy of water dissolution in low-molecular-mass esters is close to our data and is equal to 7.4–9.8 kJ/mol.<sup>21</sup> However, the affinity of water molecules for immobilizing centers decreases with the rise in temperature. The temperature dependency of K allows us to estimate the energy for the affinity of water for carbonyl groups; it was found to be close to 42 kJ/mol, which is more than three times as large as the energy of water dissolution in amorphous regions of PHB. The difference in the signs of the thermal effects testifies that water molecules arrange in different ways near polar groups and in the hydrophobic polymer matrix.

#### CONCLUSIONS

The results presented show that water equilibrium sorption and diffusion kinetics are the structure-sensitive parameters for PHB. In the range



**Figure 3** Second derivatives of absorption IR-spectra of wet (1, solid line) and dry (2, dotted line) PHB films. Absorption of free carbonyl groups and those interacting with water molecules are observed at 1747 and  $1724 \text{ cm}^{-1}$ , respectively.

of 303-333 K there is a dynamic balance between the water molecules immobilized on carbonyl groups and free water molecules dissolved in the polymer. Sorption isotherms are interpreted as a superposition of the Flory–Huggins equation and Langmuir equation for mobile and immobilized forms, respectively. The dependency of diffusion coefficients on water content was described in the framework of Fujita's immobilization model, in which the growing up function,  $D_w$  versus  $C_w$ , was characterized by the fraction of the water molecules connected with carbonyl groups. It is to be emphasized that both sorption equilibrium data and diffusion kinetic data are interpreted by application of the same coefficients [eq. (9)]. An account of transport phenomena in PHB films is essential for designing novel and environmentally friendly polymer materials.

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