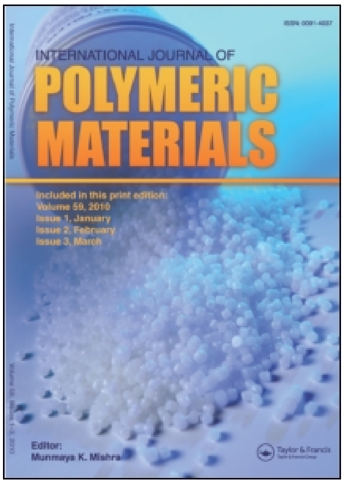

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Water Sorption and Diffusion in Poly(3-hydroxybutyrate) Films

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The temperature dependence of water vapour sorption and diffusion in poly-(3-hydroxybutyrate) (PHB) was investigated. Equilibrium sorption and diffusion kinetics were determined by a quartz Mac Bain's vacuum microbalance technique in the temperature range of 303–333 K. The water molecule interaction with the polymer matrix was analyzed for wet PHB films by FTIR spectroscopy technique. Water sorption isotherms are interpreted as a superposition of free water sorption, estimated by the Flory-Huggins equation and water immobilized on carbonyl groups of PHB. The immobilization effect was described by a Langmuir type equation. The dependence of diffusivity on water concentration was described in the framework of Fujita's immobilization model in which the growing function D_w vs C_w characterized the filling degree of carbonyl groups as sites of immobilization in the polymer. Enthalpy of free water sorption (12 kJ/mol) and water immobilization (42 kJ/mol) as well as the activation energy of water diffusion coefficients (71 kJ/mol) in noncrystalline areas of PHB were determined.

Keywords: Water; sorption; diffusion; poly(3hydroxybutyrate); films

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a representative of the class of polyhydroxyalkanoates [1]. It is characterized by a fortunate combination of high technological effectiveness [2], useful physico-chemical characteristics [indexes] [3, 4], adjustable ability to biodegradation [3, 5], and ecological compatibility with the environment [6, 7].

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This polymer is now more and more often used in medicine and veterinary science due to its satisfactory compatibility to biological media [8, 9].

PHB decomposes to carbon dioxide and water under natural conditions, under the effect of bacterias and enzymes. This makes it virtually useful for agriculture and as environment friendly pure packing material [10].

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 main aim of the present investigation is to study sorption-diffusion indexes of the PHB-water system in a wide temperature range. The broader scope is in the progress of modelling the water sorption-diffusion in moderately hydrophobic polymers.

EXPERIMENTAL

PHB films of Biomer Co., casted from chloroform, were studied in the work. They were 80±5 μm thick and possessed 70% roentgen structural crystallinity [12]. The initial polymer powder was dissolved in chloroform incompletely during a long time boiling. Its solubility was found about 0.01 g/ml. Hot solution was filtered through glassy Shott's filter. Molecular mass of the filtered substance was determined by the viscozimetry technique using the following equation [13]:

$$[\eta] = 7.7 \cdot 10^{-5} M_w^{0.82}, \qquad (1)$$

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

Mean viscous molecular weight of the polymer (M_w) was found 83.5×10^3 g/mol; according to the Table on polydispersities of the polymer shown in [13] the mean molecular weight is 3.5×10^3 g/mol.

Tests on sorption were performed by vaccum gravimetry using quartz Mac Bain's vacuum microbalance with 0.67 mg/mm sensitivity of quartz spring. The details of equipement of the sorption experiment are described elsewhere in [14].

Infrared spectra for PHB films were recorded by Bruker IFS-48-FTIR spectrometer at 2 cm^{-1} resolution and scanning number ranged from 250 to 400. Data processing of characteristic absorption spectra was performed using programs by Bruker Company.

RESULTS AND DISCUSSION

Isotherms of water vapour 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 display a specific convexity to the axis of ordinates. Each isotherm strives to a threshold value. **The** lower temperature of the experiment is, **the threshold** is observed more clearly.

To interpret sorption isotherms in analogue to the double sorption model [15], we have supposed an existence of immobilized (on polar groups, sorption centers) and free water (molecularly dissolved, possessing translational mobility) in the polymer. There exists a

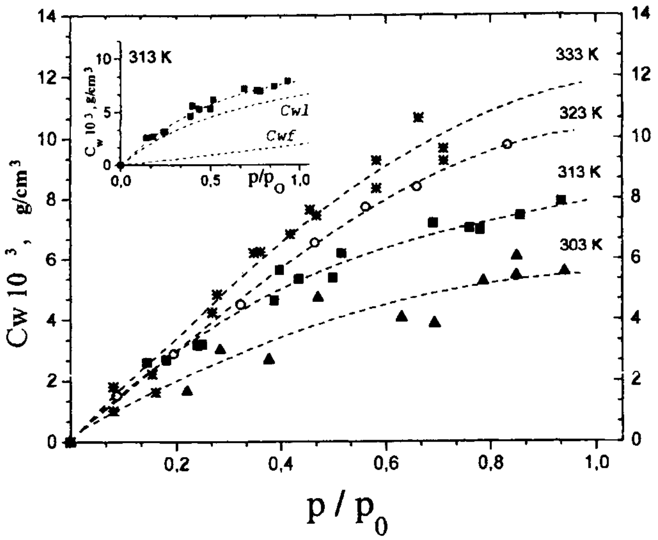

FIGURE 1 Sorption isotherms for water vapours in PHB films at different temperatures. Subdivision of the sorption isotherm into two terms at 313 K is shown as an example. See the text for details.

dynamic balance between these forms of water. Total concentration of water in the polymer may be presented as a sum of two terms:

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

Here

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

is the concentration of water sorbed according to the Henry law, i.e. the concentration of free (mobile) water. According to the Lengmuir model, the concentration of water immobilized on sorption centres in the polymer will be expressed rather traditionally as for the double sorption model:

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

Here C_H is the concentration of accessible sorption centres, K is the equilibrium constant of the Lengmuir sorption.

To estimate content of free water in PHB, we used the Flory-Huggins equation. It can be shown that at low concentration of water the Henry constant is defined by the thermodynamic parameter of solubility, χ [16]:

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

where K_H is the Henry constant from Eq. (3); χ is the Flory-Huggins constant.

The Flory-Huggins constant was obtained by the method of group contributions calculating the solubility parameter of PHB (δ_{PHB}) [11, 17] and χ for different temperatures:

$$\chi = \frac{\bar{V}_1(\mathrm{H_2O})(\delta_{\mathrm{H_2O}} - \delta_{\mathrm{PHB}})^2}{\mathrm{RT}}. \tag{6}$$

Here $\bar{V}_1(\mathrm{H_2O})$ is the fractional molar volume of water molecules; T is the absolute temperature; R is the universal gas constant.

Subdividing the experimental isotherms into the modes of free and immobilized water, we obtain the rest of parameters for Equation (4). Temperature dependences of these parameters are shown in Table I.

An example of experimental isotherm subdivision into two modes is shown in Figure 1. It displays that the concentration of free water in polymer (C_{wf}) is significantly lower than the concentration of water, linked to the sorption centres: $C_w \approx C_{wl}$.

To explain the diffusional experiments we neglected the mobility of water linked to the sorption centres of the polymer. That is why the effective flow of diffusing water in PHB observed in the experiments is promoted only by migration of free water.

In the framework of this model the expression for effective diffusion coefficients (D_{eff}) is the following [14, p. 303]:

$$D_{\text{eff}} = D_{wf}\frac{\partial C_{wf}}{\partial C_w}. \tag{7}$$

Here D_{wf} is the diffusion coefficient of water in the absentee of sorption centres in the polymer matrix.

Taking into account that free water concentration (C_{wf}) is rather low comparing with that of water, immobilized on sorption centres, we will obtain the dependence C_{wf} vs C_w basing on Eq. (7), similar to the classic expression [14, p. 304]:

$$C_{wf} = \frac{\alpha C_w}{1 - \beta C_w}, \tag{8}$$

where α and β are constants:

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

TABLE I The values of Henry (K_H) and Flory-Huggins (χ) constants, equilibrium (K) and effective sorption centre concentration (C_H) constants for the PHB-water system at different temperatures

T, K	χ	$K_H \times 10^3$, g/cm^3	$K \times 10^{-2}$, cm^3/g	$C_H \times 10^3$, 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

Solving Eqs. (7) and (8) together, one may obtain an expression for effective diffusion coefficient, which contains its dependence on concentration of sorbed water in polymer:

$$D_{\text{eff}} = \frac{\alpha D_{wf}}{(1 - \beta C_w)^2}. \tag{10}$$

An equation similar to Equation (10) was first deduced by Fujita [18].

Figure 2 shows concentrational dependences of diffusion coefficients for various temperatures. In accordance with Fujita's diffusional model, the concentrational dependence of experimental (effective) diffusion coefficients D_{eff} should be linearized in the $(D_{\text{eff}})^{-1/2} - C_w$ coordinates, which is observed in the temperature range studied.

Experimental data processing in these coordinates using the regressive analysis gave diffusion coefficients for "free" water (i.e. water molecules, which migrate in the polymer matrix in the absence of sorption centres). It should be noted that the values of diffusion constants α and β, used in Eq. (10), were obtained from the equilibrium sorption data, i.e. by an independent experiment. The values of D_{wf} are shown in Table II.

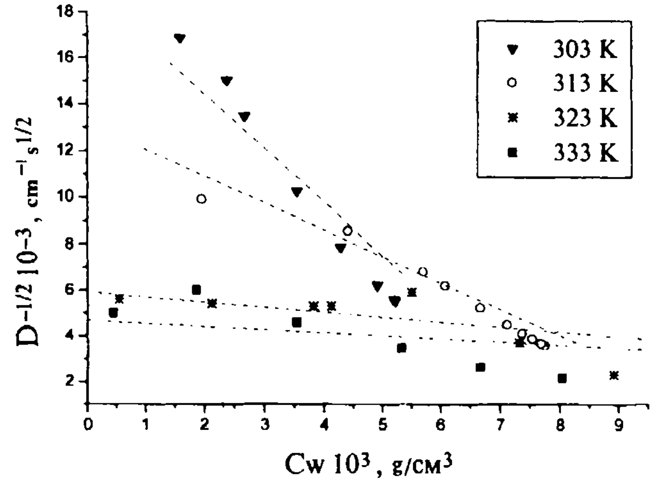

FIGURE 2 Concentrational dependences of water diffusion coefficients in PHB at different temperatures in the coordinates of Eq. (10). Dotted lines mark calculated values, points mark the experimental data.

TABLE II Water diffusion coefficients in PHB at different temperatures

T, K	$D_{wf} \times 10^8$, cm^2/s	$D_{w\ \mathrm{eff}(C \to 0)} \times 10^9$, cm^2/s
303	1.6	2.3
313	4.5	10
323	18	33
333	28	37

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 defined, first of all, by existence of carbonyl groups in PHB, capable for forming hydrogen bonds with the molecules of water. Previous results [19] displayed a possibility for proceeding of such interactions with the formation of cyclic structures in polymer with participation 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 [17, 19] is confirmed by recorded IR-spectra, from which the second derivative of absorption intensity in the range of 1749 – 1722 cm^{-1} were built (see Fig. 3). This Figure shows the results of water interaction with carbonyl groups in PHB, and as a

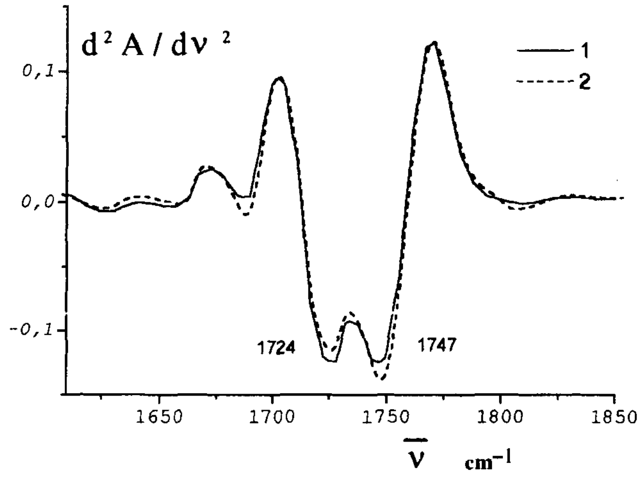

FIGURE 3 Second derivatives of absorption IR-spectra of wet (1) and dry (2) PHB films. Absorption of free carbonyl groups and those interacting with water molecules are observed at 1747 and 1724 cm^{-1}, respectively.

consequence, an increase of the peak intensity of carbonyl groups (1724 cm $^{-1}$) and decrease of the peak intensity of free carbonyl groups (1747 cm $^{-1}$), i.e. transition of carbonyl groups from the free state into the state bound to water molecules.

The analysis of the temperature dependence of free water diffusion coefficients and effective diffusion coefficients, extrapolated to the zero diffusant concentration ($D_{w\,\mathrm{eff}(C\to 0)}$) (see Tab. II), shows that activation energies of diffusion are rather high (71 – 84 kJ/mol). Probably, so high activation energies make formation of the diffusion activation volume in highly crystalline matrix of PHB difficult.

Analyzing temperature dependences of the equilibrium sorption parameters from Table I, one may note that the solubility coefficient (the Henry constant) of free water grows with temperature. Heat of water dissolution in PHB matrix is quite low and equals to 12 kJ/mol. Low heat effect of sorption is also characteristic for other polymers possessing moderate hydrophobity [20]. Let us note that the enthalpy of water dissolution in low molecular esters is close to that found by us and range within 7.4 – 9.8 kJ/mol [21]. At the same time, the affinity of water to immobilizing centres vice versa decreases with the temperature increase. Temperature dependence of K allows to estimate the energy of water affinity to carbonyl groups. It is close to 42 kJ/mol, which is more than three-fold higher than the energy of water dissolution in amorphous regions of PHB. Different signs of heat effects testify a principal difference in the nature of water dislocation near polar groups and in hydrophobic polymer matrix.

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