



# The characterization of novel biodegradable blends based on polyhydroxybutyrate: The role of water transport<sup>☆</sup>

Yu.N. Pankova<sup>a</sup>, A.N. Shchegolikhin<sup>b</sup>, A.L. Iordanskii<sup>a</sup>, A.L. Zhulkina<sup>a</sup>, A.A. Ol'khov<sup>c</sup>, G.E. Zaikov<sup>b,\*</sup>

<sup>a</sup> N. Semenov's Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

<sup>b</sup> N. Emanuel's Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

<sup>c</sup> D. Mendeleev's Academy of Fine Chemical Technology, Moscow, Russia

## ARTICLE INFO

Available online 4 May 2010

### Keywords:

Polyhydroxybutyrate (PHB)

Water permeability

Kinetics

Diffusion

Blends

Biodegradation

## ABSTRACT

The present paper focuses on the study of novel blends based on poly(3-hydroxybutyrate) (PHB) and polymers with different hydrophilicity, namely low density polyethylene and polyamide (LDPE and PA), respectively. Polymer blends were produced from five ratios of PHB/LDPE in an effort to regulate the resistance to hydrolysis or (bio) degradation through the control of water permeability. The relation between the water transport and morphology (TEM data) shows the impact of polymer component ratio on the water flux regulation in the hydrophobic matrix. To elucidate the role of hydrophilicity of the second component present in the PHB-based blends, we studied the PHB/PA blends where PA is the polyamide resin composed of statistical copolymer of hexamethylenedipic acid and  $\epsilon$ -caprolactam in the ratio 1:1. The use of techniques such as DSC and FTIR-imaging (for T-scale) demonstrates the interaction between PHB and PA in the temperature ranges of crystallization and melting. The general approach based on Flory–Huggins equation is presented as the way to choose the pairs of compatible or partly compatible polymers. Blending PHB with PA could be a simple and effective method to design new matrices for drug delivery in medicine, while the same procedure applied for PHB-LDPE system with better resistance against hydrolysis and lower price than the initial PHB, could be used as novel bioerodible packaging materials.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

The families of biodegradable polymers, namely poly- $\alpha$ -hydroxyacids (PLA, PGA, and their copolymers, PLGA) as well as poly- $\beta$ -hydroxyalkanoates (PHA): poly(3-hydroxybutyrate) (PHB) and its copolymers, especially with hydroxyvalerate (PHBV), have very good performance characteristics. Their characteristics are sufficient to replace a significant portion of petroleum-based plastics used currently in medicine, packaging and food-service industry [1–3]. Along with biodegradability, the PHAs and their principal member PHB are biocompatible and environmental friendly [4–6]. In living organism and soil their macromolecules decompose to form the nontoxic intermediates and final products included in carbohydrate metabolism. Besides, bacterial PHB and its copolymers have also proved to be useful as model materials for investigating physical properties such as crystallization and diffusion.

However, the mechanical deficiency, a narrow processing window as well as the high cost of PHB/PHA, restricts its application as a

friendly environmental biomedical material. For the solution of the above-mentioned three problems, we propose the specific blending of PHB, as a pivotal component, and a set of synthetic (LDPE and polyamide-66) polymers, with a different macromolecule polarity to design the (bio) degradable blends/compositions with improved transport and physical characteristics, which are useful for the development of packaging, biodegradation [7], and drug delivery [8].

## 2. Experimental

In the current study, we used PHB in the powder form which was kindly supplied by Biomer Co Kraling (Germany) Lot #216 with  $M_w = 206$  kDa, density  $1.248$  g/cm<sup>3</sup>. The blend films were produced using a) the low density polyethylene (LDPE), namely the commercial product (RF 15803-020 grade) in the form of granules with  $M_n = 2.0 \times 10^5$  Da; and b) the polyamide resin composed of statistical copolymer of hexamethylenedipic acid and  $\epsilon$ -caprolactam in the ratio 1:1 with  $M_n = (1.94 \pm 0.06) \times 10^4$  Da and containing 38% of amide groups, with a content of terminal groups equals  $(5.0 \pm 0.1) \times 10^{-2}$  mol/kg for  $-\text{NH}_2$  groups and  $(5.3 \pm 0.1) \times 10^{-2}$  mol/kg for  $-\text{COOH}$  groups. The blends were prepared by solvent casting from chloroform-ethanol solvent combination (both solvents of medical grade quality) and by melt/solid extrusion with a single-screw extruder. A series of LDPE-PHB

<sup>☆</sup> Dedicated to Professor Victor Lobo on the occasion of his 70th birthday.

\* Corresponding author. N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin str., Moscow 119334, Russia. Tel.: +7 495 939 73 20; fax: +7 495 137 41 01.

E-mail address: [chembio@sky.chph.ras.ru](mailto:chembio@sky.chph.ras.ru) (G.E. Zaikov).

blends was prepared with the following component ratios (w/w): 68:32, 84:16, 92:8, 96:4, and 98:2.

FTIR spectra of the blend films were recorded with the spectrometer “Bruker IFS-48” (Germany) at resolution  $2\text{ cm}^{-1}$  being the number of the scans about 70. Computer analysis of final spectra has been performed with the in-built programs in the range  $500\text{--}3500\text{ cm}^{-1}$ . A Perkin-Elmer differential scanning calorimeter (Model DSC7), calibrated with indium, was applied for the study of the thermal behavior of PHB-PA blends, as well as for pure polymers (PHB and PA) separately. Specimens of about 5 mg were encapsulated in aluminium pans and heated/cooled at a constant rate  $10\text{ }^\circ\text{C}/\text{min}$ . The range of heating includes a temperature interval from room temperature to  $182\text{ }^\circ\text{C}$ . The enthalpies of fusion  $\Delta H_{\text{PHB}}$  for PHB and  $\Delta H_{\text{PA}}$  for PA were measured to calculate the crystallinity degrees  $\alpha_{\text{PHB}}$  and  $\alpha_{\text{PA}}$  using the following equations.

$$\alpha_{\text{PHB}}(\%) = [\Delta H_{\text{PHB}} / \Delta H_{\text{PHB}}^0 (1 / w_{\text{PHB}})] 100 \quad (1)$$

$$\alpha_{\text{PA}}(\%) = [\Delta H_{\text{PA}} / \Delta H_{\text{PA}}^0 (1 / w_{\text{PHA}})] 100 \quad (2)$$

where  $w_i$  ( $i = \text{PHB}$  or  $\text{PA}$ ) is the weight fraction of each component in the blend, and  $\Delta H_{\text{PHB}}^0$  and  $\Delta H_{\text{PA}}^0$  are the enthalpies of fusion of completely crystalline polymers PHB ( $87\text{ cal/g}$ ) and PA ( $54\text{ cal/g}$ ), respectively [9].

### 3. Results and discussion

#### 3.1. General approach in framework of Flory–Huggins theory

The analysis of water solubilities in accessible intercrystalline area for about 50 polymers with different chemical structures (hydrophilicity) indicates that the classification of such polymers can be performed by a combination of the modified Flory–Huggins equation (at  $a_w = 1$ ) with an expression for the solubility parameter in the framework of the regular solution model [10] (Eqs. (3) and (4), respectively)

$$\ln \varphi_w + \varphi_p + \chi_{wp} \varphi_p^2 = 0 \quad (3)$$

$$\chi_{wp} = \frac{\bar{V}_w}{RT} (\delta_w^2 - \delta_p^2) \quad (4)$$

Inserting expression of  $\chi_{wp}$  in Eq. (3), the following final equation is achieved:

$$\ln \varphi_w + \varphi_p + \frac{\bar{V}_w}{RT} (\delta_w^2 - \delta_p^2) \varphi_p^2 = 0 \quad (5)$$

where  $\varphi_w$ ,  $\varphi_p$  are the volume fractions of water and polymer, respectively, and  $\delta_i$  are the solubility parameters of water (W) and polymer (P),  $\chi_{wp}$  is the Flory interaction parameter,  $\bar{V}_w$  is the molar volume of water,  $R$  is the gas constant and  $T$  is the absolute temperature.

The plot of Flory–Huggins equation (at water activity,  $a_w = 1$ ) using coordinates  $(\ln \varphi_w + \varphi_p)$  vs.  $(\delta_w^2 - \delta_p^2) \varphi_p^2 \equiv Z$  is generally non-linear and can be approximated by two intersectional lines in intervals:  $Z \leq 600\text{ J}/\text{cm}^3$  for the hydrophilic polymers (poly(vinyl alcohol) – PVA, cellulose, chitosan and the like), and  $Z \geq 800\text{ J}/\text{cm}^3$  for the hydrophobic polymers (as for example, LDPE, high density polyethylene – HDPE, polypropylene, polystyrene and rubbers), see Fig. 1. The points located in the vicinity of the intersection point of the above lines, at  $600 < Z < 800\text{ J}/\text{cm}^3$ , belong to the moderately hydrophilic polymers [11].

In Fig. 1 the water equilibrium sorption in the above systems of coordinates is presented. Two polymers (PHB and PHBV) from the

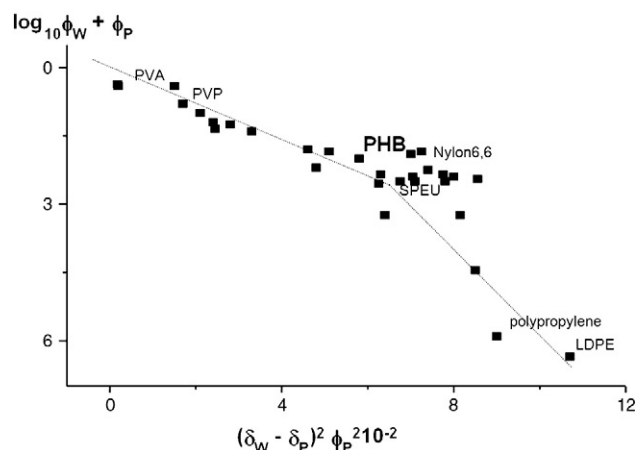


Fig. 1. The pattern of water solubility in polymers with different hydrophilicity [11] in framework of Flory–Huggins equations.

family of polyhydroxyalkanoates with Hildebrand solubility parameters  $\delta_p = 19.8$  and  $19.4\text{ J}^{1/2}/\text{cm}^{3/2}$  ( $\text{Pa}^{1/2}$ ) [12], respectively, are situated in the vicinity of the intersection point. Data related to 55 polymers with different hydrophilicity have been collected by our group [13]. Variation of second polymer polarity in its blend/composite with the PHB (PHBV) regulates composite morphologies and, hence, both water and drug transport as well as thermophysical and mechanical behavior of polymer systems. Here we initiate our consideration with the description of an utmost situation where the PHB has been combined with typical hydrophobic polymer–polyethylene (LDPE).

Analyzing the micrographs obtained in a preliminary paper of our group [14], we can distinctly discern the porous space between continuous medium of the major phase of LDPE and the band-like fibrils of PHB. These materials have a microscopically complex structure with random distribution of pore sizes, ranging from a few micrometers to tens of micrometers. In packaging or pharmaceutical practice, in order to regulate the water permeability, the structure is slightly affected by an external force aroused during a film preparation or exploitation. Thus, controlling optimal values of the composite parameters such as porosity, permeability and hydrophilicity, are important issues in polyhydroxybutyrate–polyethylene research.

#### 3.2. Transport behavior of water in blend of PHB with hydrophobic polymer (PELD)

The total water permeability of the LDPE/PHB blends ( $P_w$ ) can be described by the equation:

$$P_w = a_s^{\text{PE}} F_{\text{PE}} P_w^{\text{PE}} + a_s^{\text{PHB}} F_{\text{PHB}} P_w^{\text{PHB}} + a_s^{\text{Int}} P_w^{\text{H}} \quad (6)$$

where  $P_w^{\text{PE}}$ ,  $P_w^{\text{PHB}}$  and  $P_w^{\text{H}}$  are the water permeabilities in the phases of LDPE and PHB, and through the interphase, respectively;  $\alpha_s^{\text{PE}}$ ,  $\alpha_s^{\text{PHB}}$  and  $\alpha_s^{\text{Int}}$  ( $\alpha_s^{\text{Int}} = 1 - \alpha_s^{\text{PE}} - \alpha_s^{\text{PHB}}$ ) are the fractions of the film cross section possessed by the phase of each component and interphase;  $F_{\text{PE}}$  and  $F_{\text{PHB}}$  are the functions characterizing the orientation impact of the polymeric segments on the water permeability in the phases of LDPE and PHB respectively. In accordance with scanning electron microscopy results [14], the porous structure in the interphase is formed and, hence,  $P_w^{\text{H}}$  is equal to the hydraulic permeability [15]. Here, the porous medium is modeled as a continuum, composite material and its structure is characterized with a minimal set of properties, namely the porosity ( $\alpha_s^{\text{Int}}$ ) and the hydraulic permeability ( $P_w^{\text{H}}$ ), which might be functions of position (architecture) and structural element orientation (anisotropy)

Download English Version:

<https://daneshyari.com/en/article/5412944>

Download Persian Version:

<https://daneshyari.com/article/5412944>

[Daneshyari.com](https://daneshyari.com)