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## MORPHOLOGY AND PROPERTIES OF BLENDS OF POLY(3-HYDROXYBUTYRATE) WITH POLY(VINYL ALCOHOL)

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**Abstract.** The structure of extruded films based on blends of polyvinyl alcohol and poly(3-hydroxybutyrate) (PHB) was studied for various compositions. The methods of DSC and X-ray analysis were used. As the phase-sensitive characteristics of the composite films, diffusion and water vapor permeability were also investigated. In addition, the tensile modulus and relative elongation-at-break were measured. Changes in the glass transition temperature of the blends and constant melting points of the components show their partial compatibility in intercrystallite regions. At the content of PHB in the composite films equal to 20–30 wt % their mechanical characteristics and water diffusion coefficients are dramatically changed. This fact, along with the analysis of the X-ray diffractograms, indicates a phase inversion in the above narrow concentration interval. The complex pattern of the kinetic curves of water vapor permeability is likely to be related to additional crystallization, which is induced in the composite films in the presence of water.

**Keywords:** morphology, poly(3-hydroxybutyrate), blend, polyvinyl alcohol, diffusion.

### 1. Introduction

To vary the physicochemical, mechanical, and diffusion characteristics of the polyvinyl alcohol (PVA) and to widen the area of its practical application [1-3] mixed compositions with a moderately hydrophilic polymer were proposed [4].

To improve the mechanical behavior of PHB and simultaneously to lower the cost of its production the modification can be made through the PHB blending with other relevant polymers. Resulting polymer blends are potentially able to gain the properties different from the ones of parent blend-forming polymers.

Poly(3-hydroxybutyrate) (PHB) was used as the modifying polymeric component. The selection of this polymer is due to its biocompatibility with animal tissues and blood. Taking into account similar properties of PVA, one may expect that a new class of polymer materials for medical purposes will be created [5, 6].

A widespread procedure for regulating the drug release rate involves controlled changes in the balance of hydrophilic interactions in the polymer matrix at the molecular level. Therefore, regulation of structural organization at the molecular and supramolecular levels makes it possible to control the rate of drug delivery and hence to improve the therapeutic efficacy of new medicines.

### 2. Experimental

We studied the PVA (trade mark 8/27, Russia) containing 27 % VAc;  $M = 3.8 \cdot 10^4$ . The corresponding DSC curve shows two melting peaks at 403 and 443 K. As the other component, we used powdered PHB (Lot M-0997, Biomer, Germany) with  $M = 3.4 \cdot 10^5$ , melting point 449 K, and the degree of crystallinity 69 % (X-ray) or 78 % (DSC).

The mechanical mixtures were prepared in the following proportions PVA:PHB = 100:0, 90:10, 80:20, 70:30, 50:50, and 0:100 wt %. The as-prepared mixtures were processed into films with the thickness of  $60 \pm 5$   $\mu$ m using an ARP-20 single-screw extruder (Russia) with a screw diameter of 20 mm and the diameter-to-length ratio of 25. In the extruder zones, the temperature was varied from 423 to 463 K.

The structure of the as-prepared films was characterized by DSC methods on a Mettler TA-4000 indium-calibrated thermal analyzer; the scanning rate was 20 K/min. The structure of the test samples was also

characterized by X-ray analysis on an automated X-ray diffractometer (CuK $\alpha$ -radiation,  $\lambda = 0.154$  nm) with a linear coordinate detector (Joint Institute for Nuclear Research, Chernogolovka) [7].

The tensile modulus and relative elongation-at-break of the composite films were estimated using a ZE-40 tensile machine (Germany) at a cross-head speed of 100 mm/min; the gage width of the test samples was 10 mm. The water vapor permeability of the composite films was measured according to the standard beaker method [8] at  $296 \pm 1$  K and a saturated water vapor pressure of 2.8 kPa; the results were taken from five parallel experiments. The accuracy of weighing was equal to  $\pm 0.001$  g.

### 3. Results and Discussion

The results of DSC studies of the composite films based on the PVA copolymer and PHB are summarized for various film compositions in Fig. 1 and in the Table below. As is seen, the average glass transition temperature  $T_g$  of the blends lies between 297 and 327 K, the values corresponding to the glass transition temperatures of the starting PHB and PVA. This fact indicates a mixing of segments of these macromolecules in amorphous regions. The changes in  $T_g$  of the composites with respect to  $T_g$  of the starting polymers clearly indicate the compatibility of the components. However, the presence of a crystalline phase in both components at various content ratios suggests a limited interaction between the polymers.

Analysis of the nature of the double peak in the DSC melting curve of the PVA samples is beyond the scope of this work. However, one may attempt to explain this fact on the basis of published data [9-11].

This behavior may be related to a wide size distribution of crystallites, as well as to their metastable character. As was asserted in Ref. [10], the typical DSC curves of crystalline polymers show several melting peaks; their height and position on the temperature axis are controlled by the temperature-time conditions of the sample processing in the extruder.

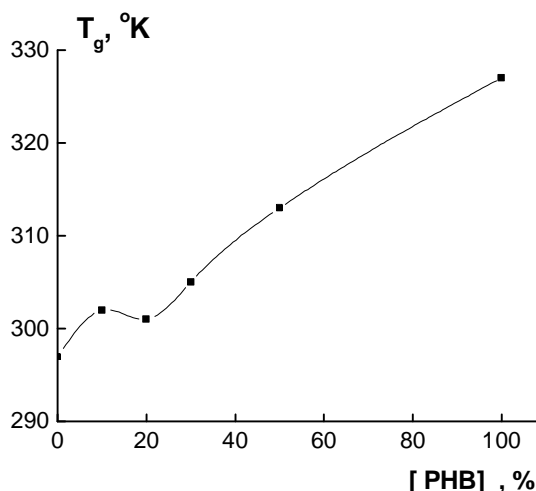


Fig. 1. Dependence of glass transition temperature of blending films from concentration of PHB

The presence of the double peak in the DSC curves of the PVA films may also be explained by the effect of extrusion-induced orientation, which may lead to the development of various morphological structures with different temperatures of phase transitions. As was stated in Ref. [11], polymers may have various crystalline modifications with identical crystallographic parameters of the unit cell but different energy levels.

As was found, the positions of the high-temperature and low-temperature peaks in the DSC curves, which correspond to the melting points of the starting components, are almost independent of the blend composition and remain invariable in the whole concentration range under study (Table). However, the transient region characterizing the glass transition temperature of the PVA-PHB system assumes different positions on the temperature axis depending on the concentration of PHB. This situation is vividly illustrated in Fig. 1, where  $T_g$  of the blend is seen to increase with the content of PHB.

Table

Characteristics of the composite films based on PVA and PHB

PVA:PHB, %	$T_m$ , K	* $P_w \cdot 10^8$ , g·cm/cm <sup>2</sup> ·h·Pa	** $C_w \cdot 10^3$ , g/cm <sup>3</sup> ·Pa
100:0	402/443	2.1	0.28
90:10	396/459	0.56	0.068
80:20	403/443	0.79	0.023
70:30	405/448	0.86	0.0075
50:50	405/451	0.94	0.01
0:100	449	0.0025	$7.5 \cdot 10^{-4}$

Notes: two melting temperatures ( $T_m$ ) of the composite films correspond to the two peaks in the DSC heating scans; \* – water vapor permeability coefficient; \*\* – water solubility coefficient.

To reveal the morphology of crystalline regions in the composite films, the DSC measurements were combined with an X-ray study. As was shown for the entire composition range under study, the quasi-crystalline phase of the PVA copolymer is characterized by a well-pronounced orientation of the macromolecular axes along the texture axis, which coincides with the extrusion direction: the (110) X-ray reflection is located on the equator (Fig. 2a). In the crystal lattice of the PVA copolymer, the normal to the (110) plane is perpendicular to the  $c$  axis, along which the axes of macromolecules are oriented. In samples containing 10 and 20 % PHB, the crystalline phase of PHB is almost fully oriented. In this case, the (020) reflection is located on the equator. The normal to the (020) plane is the  $b$  axis, and the  $a$  axis coincides with the direction of the film extrusion. The  $c$  axis of the unit cell of PHB, which is parallel to the directions of macromolecules, is perpendicular to the extrusion direction.

X-ray diffractograms of films containing 30 % and more PHB show the presence of the isotropic phase of PHB in appreciable amounts (Fig. 2b). The parameters of the unit crystal cells of the polymers in the blends were estimated. The crystalline phase of PHB is shown to be characterized by an orthorhombic unit cell:  $a = 0.576$ ,  $b = 1.32$  and  $c = 0.596$  nm [10]. The crystalline phase of the PVA in the quasi-crystalline modification includes regions with a close packing of parallel chains (the  $\gamma$  modification); the parameters of the unit cell are:  $a = 0.78$ ,  $b = 0.253$  and  $c = 0.549$  nm [12]. In the corresponding X-ray diffractograms, these regions are associated with an X-ray reflection at  $S = 2.22$  nm<sup>-1</sup>.

The data of X-ray analysis allow one to conclude that the crystal lattice parameters of the components of the composite films are invariable; only the content of the isotropic component of the crystalline PHB phase is changed in the region of the phase transition.

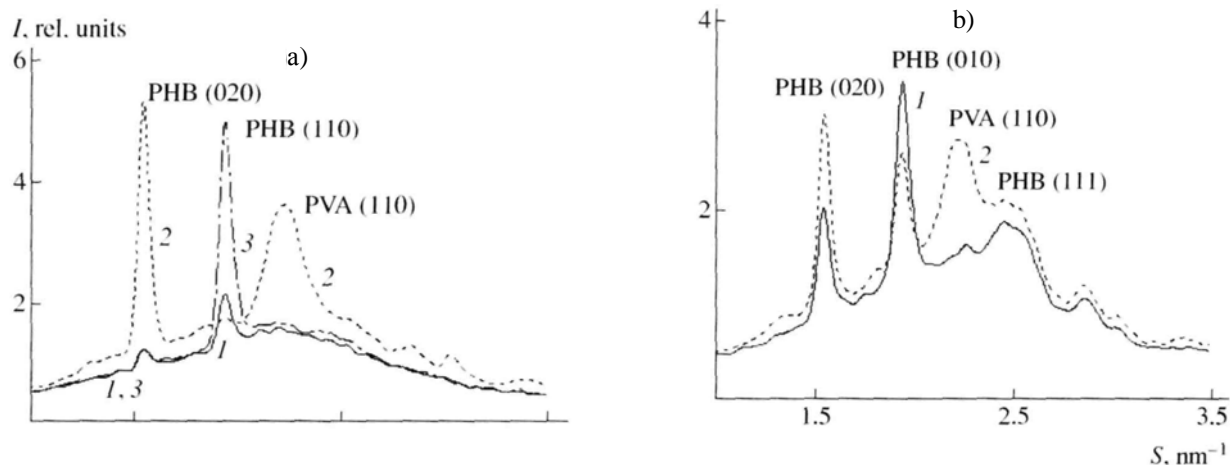
The results of mechanical tests of the PVA-PHB composites (uniaxial tension) fully support the above conclusion that phase inversion takes place in the films containing 20–30 % PHB. This reasoning is proved by an abrupt inflection in the dependences of the tensile strength  $\sigma_t$  (Fig. 3, curve 1) and elongation-at-break  $\varepsilon_t$  (Fig. 3, curve 2) on the composition of the blends, as well as by the presence of a minimum in the dependence of the tensile modulus  $E_t$  (Fig. 4) on the composition of the composite films.

According to the data presented in Figs. 3 and 4, the properties of the composite films are controlled by the PVA matrix when the concentration of PHB is below 20 % but determined by the PHB matrix at a concentration of 30 % PHB and higher.

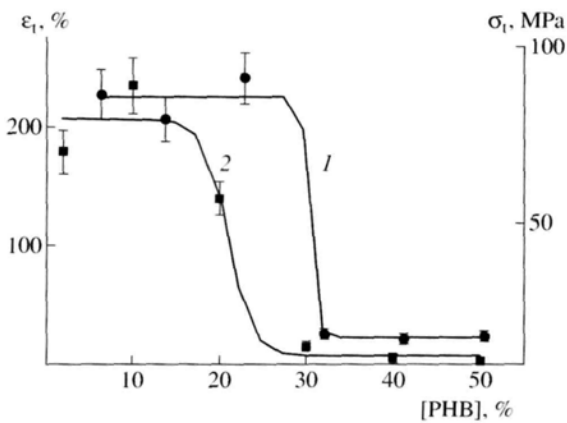
Almost invariable  $\sigma_t$  and  $\varepsilon_t$  values of the composite films before and after the phase inversion region may be explained as follows: particles of the dispersed phase do not serve as stress-concentrating sites in the matrix. This situation is possible when the dispersed phase is uniformly distributed within the matrix and the dimensions of its particles are rather small. This is usually observed in the case of a complete or partial miscibility of the polymer components [13, 14].

Let us consider the process of water vapor transfer through the PVA-PHB composite films.

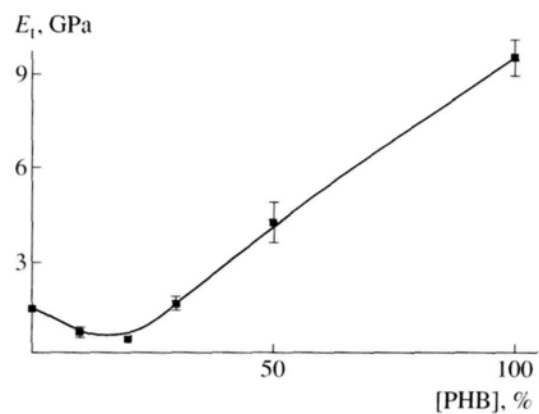
Fig. 5 presents the kinetic curves of vapor permeability for various PHB contents. One may distinguish three characteristic portions in these curves. The initial portion refers to a non-steady-state transport mechanism (Fig. 5b). In this region, the diffusion flow depends on time because the diffusion is related to the physical-chemical process of the binding of water molecules on functional groups of PHB, which show a marked affinity to water (carbonyl groups [14], acetate and hydroxyl groups of the PVA [15,16]).



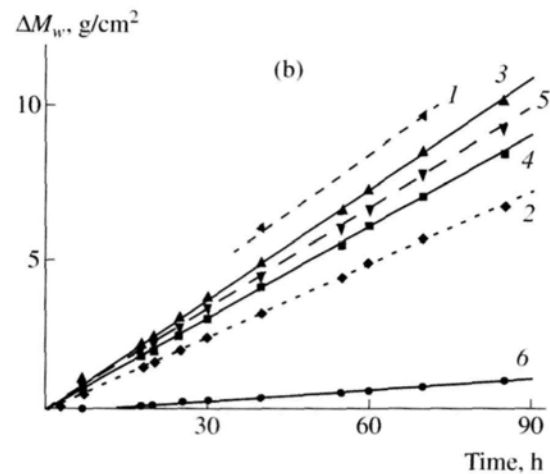
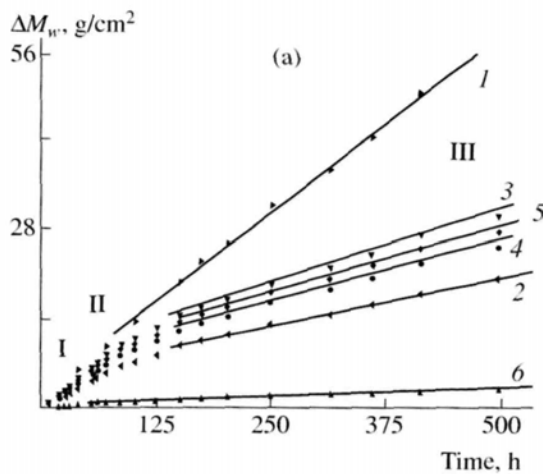
**Fig. 2.** X-ray diffractograms of the films with a composition of 80:20 (a) and 70:30 (b) wt % recorded along the orientation axis (1) and at the angle of 90° (2) or 20° (3) to the orientation axis.  $S = 2\sin\theta/\lambda$ , where  $\theta$  is the X-ray scattering angle and  $\lambda$  is the wavelength



**Fig. 3.** Tensile strength  $\sigma_t$  (1) and relative elongation-at-break  $\epsilon_t$  (2) of the composite films vs. content of PHB



**Fig. 4.** Tensile modulus  $E_t$  of the composite films vs. content of PHB



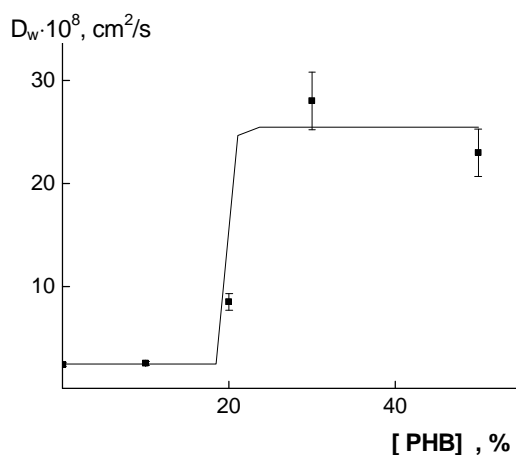
**Fig. 5.** Kinetic curves of water vapor permeability per unit area of the composite films with the following compositions: 100:0 (1); 90:10 (2); 70:30 (3); 80:20 (4); 50:50 (5) and 0:100 (6). The Roman numerals refer to the three characteristic regions discussed in the text: general pattern (a) and initial fragment of the kinetic curves (b)

The next (middle) portion in the kinetic permeability curves corresponds to quasi-steady-state transport, where the segmental mobility of PVA increases under the action of the diffusing water and an additional crystallization of the hydrophilic component is likely to occur [17]. Such phenomena were described in detail and analyzed in [18]. As the degree of crystallinity in the composite films increases, the rate of the effective flow of the diffusing component must decrease, and this trend is well seen in the last portion of the kinetic curves (Fig. 5a). Since newly formed crystallites are impermeable to water and therefore create an additional diffusion resistance, the slope of the last portion of the kinetic curves markedly decreases compared to the slope of the curves in the preceding portion.

The dependence of diffusion coefficients on the composition of the polymer blend (Fig. 6) shows a characteristic inflection at a content of 30 % PHB, which corresponds to the phase inversion of the polymer matrix. In this region, one may observe an abrupt decrease in the tensile strength and relative elongation-at-break (Fig. 3). Strictly speaking, the traditional interpretation of diffusion equations in this region seems to be poorly justified and requires a detailed analysis, including consideration of the convective transfer mechanism [19]. The correlation between the transport and mechanical characteristics of the films indicates the important role of structural and morphological elements of the PVA-PHB mixed compositions.

The Table lists the vapor permeability and solubility coefficients for the initial polymers (PVA and

PHB) and composite films of various compositions estimated by the Daynes-Barrer method [20]. As follows from the Table, the solubility coefficient  $C_w$  monotonically decreases with the increasing concentration of PHB. This result seems to be quite evident, since the amount of sorbed water depends on the nature and concentration of functional groups in the polymer.



**Fig. 6.** Water vapor diffusion coefficients  $D_w$  of the composite films vs. content of PHB

The coefficient of water vapor permeability slightly depends on the composition of the blends. Since this parameter is controlled by diffusion, equilibrium water sorption, and structure of the films at the crystal level, the interpretation of the results is ambiguous. For example, the above decrease in the solubility may be compensated by a structural amorphization of the components of the composite films near the phase inversion point.

As the content of the PVA copolymer in the polymer blend is increased, the concentration of hydroxyl groups evidently rises. The hydrophilization of the PHB matrix (with increasing content of the PVA component) provides a monotonic increase in the water solubility coefficient without any visible inflection points and extrema (see Table). Even though the films may experience various structural rearrangements at the crystal level, as is evidenced by the DSC data, X-ray analysis, and mechanical tests, the water solubility in the PVA-PHB composite films is still sensitive only to changes in the ratio between the contents of the hydrophilic and moderately hydrophilic components. Therefore, the content of dissolved water is controlled by the nature and concentration of functional groups in the polymer blend.

As the content of PHB in the blends is increased, the concentration of hydroxyl groups decreases; that is, at the molecular level, hydroxyl groups with their high group contribution (according to van Krevelen) are substituted

by ester groups of PHB with a much lower group contribution [21].

## 4. Conclusions

A blend designed on the basis of polymer components with essentially different hydrophilicity is of academic and industrial interest, primarily, for the control of such critical but scantily known characteristics as water permeability, equilibrium sorption, and diffusional mobility.

In spite of limited concentration interval of partly miscible blending (no more than 30 wt % of PHB) these PHB-PVA blends are of great interest as novel biodegradable films and coatings. Additionally, the blends based on water-soluble and biocompatible PVA and environmentally friendly and biocompatible PHB could be treated as new generation of environmentally friendly materials in packaging industry, agricultural application as well as biomedicine areas [22-24].

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### МОРФОЛОГІЯ І ВЛАСТИВОСТІ СУМІШЕЙ НА ОСНОВІ ПОЛІ(3-ГІДРОКСИБУТИРАТУ) ПОЛІВІНІЛОВОГО СПИРТУ

*Анотація.* Вивчено морфологію екструзійних плівок на основі сумішей полівінілового спирту (ПВС) і полі(3-гідроксибутирату) (ПГБ) при різних співвідношеннях компонентів. Для аналізу застосовано методи ДСК і рентгеноструктурного аналізу. Досліджено дифузійні характеристики (коефіцієнт дифузії та паропроникність води) і фізико-механічні властивості (модуль пружності при розтягненні і відносно подовження при розриві) як фазочутливі параметри сумішевих плівок. Показано, що зміни температур склування і топлення компонентів суміші вказують на часткову сумісність у міжкристалічних (аморфних) областях. Виявлено, що в області концентрації ПГБ 20–30 % мас. механічні характеристики і коефіцієнти дифузії різко змінюються. Експериментальні результати разом з аналізом рентгенівських дифрактограм вказують на інверсію фаз ПВС і ПГБ у приведеному вище інтервалі концентрації ПГБ. Показано, що складний характер кінетичних кривих паропроникності у сумішах може бути пов'язаний з додатковою кристалізацією ПГБ, яка прискорюється в присутності води.

*Ключові слова:* морфологія, полі(3-гідроксибутират), суміш, полівініловий спирт, дифузія.