

# Water Transport, Structure Features and Mechanical Behavior of Biodegradable PHB/PVA Blends

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## INTRODUCTION

In recent decades, bacterial poly(3-hydroxybutyrate) (PHB) and related bacterial polyhydroalkanoates (PHAs) have attracted much attention as biodegradable and bio-compatible materials with potential applications in packaging, agricultural, as well as medical areas.<sup>1,2</sup> In contrast to synthetic polymers, PHAs including PHB have the essential advantage of being renewable resources without the use of petrochemical feedstock. Moreover, this class of polymers are biodegradable, that is, PHAs can be completely digested and metabolized by a wide variety of bacteria and fungi in a living body or soil and in other environments.<sup>3-5</sup>

To improve the mechanical behavior of PHB and simultaneously to depress expenditures in its production, the modification can be made through blending PHB with other relevant polymers. The resulting polymer blends are potentially able to gain properties different from the properties of parent blend-forming polymers. In contradistinction to traditional biodegradable polymer blends, such as starch-based plastics, PHAs possess a useful combination of transport and mechanical characteristics.

This work was devoted to the study of water diffusion in PHB–poly(vinyl alcohol) (PVA) blends and the determination of the relationship between transport parameters and mechanical properties of these blends. Recently, some authors<sup>6</sup> studied PVA–PHB blends prepared by casting from the solvent, dissolving both polymers simultaneously. They found that the structures of these polymers changed and the crystallinity for each polymer decreased. It is worthwhile to note that the preparation of PVA–PHB blends via solution casting is poor as a technological method if compared with melt extrusion. Moreover, the use of solvents is a serious hazard to human health and environment protection. This procedure also demands additional energetic and material expenses to regenerate the solvent

used. On this basis, we studied the properties of PVA–PHB blends obtained by extrusion of the two-component polymer melts.

## EXPERIMENTAL

This study was concerned with PVA 8/27 (Russian trade mark) and PHB (Biomer, Krailing, Germany, Lot M-0997). The residual acetate group concentration and Na acetate salt concentration in PVA comprise 8.2 and 0.04% wt, respectively. The molecular weight of PVA is 64,000g/mol with a melting point of 146°C. The main characteristics of PHB are a molecular weight of 340,000,  $T_m$  of 178°C (DSC data), and a crystallinity degree of 78% (DSC) or 69% (X-ray technique).

### Blending

The loaded concentration of PVA:PHB ingredients varied as 100:0, 90:10, 80:20, 70:30, 50:50, and 0:100. The blends were produced using a single-screw extruder, an ARP-20 with  $L/D = 25$  and diameter = 0.20 cm. Electricity heating was used to obtain a 180°C flat-extrusion profile. The components were first premixed in a Brabender Plasticorder PCE330 at 170°C and at a 60-rpm rotor speed after drying the ingredients in an air oven at 101°C for 8 h. The screw rotation was 100 rpm. The films were obtained with a final thickness of 60  $\mu\text{m}$  and were air-cooled to room temperature.

Characteristics of the films were studied by a DSC technique with a Metler PR4000 calorimeter at a heating rate 20°/min and wide-angle X-ray scattering (WAXS) in two different directions: parallel and normally to film surface. Details of the X-ray measurements were described elsewhere.<sup>7</sup> The tensile modulus and elongation at break of the films were determined from measurements on an Instron 1122 tensile apparatus. The drawing speed was 1.0 cm/min and the results were averaged from at least five tests.

### Water-vapor permeability experiments

Water-vapor permeation was measured at 23°C using the a regular two-compartment cell especially desig-

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**TABLE I**  
Glass Transition Temperatures of Blends with Different Contents of PHB

Measurement	PHB content (% wt)					
	0	10	20	30	50	100
$T_g$ (°C)	53.9	32.7	28.5	25.3	25.9	24.1

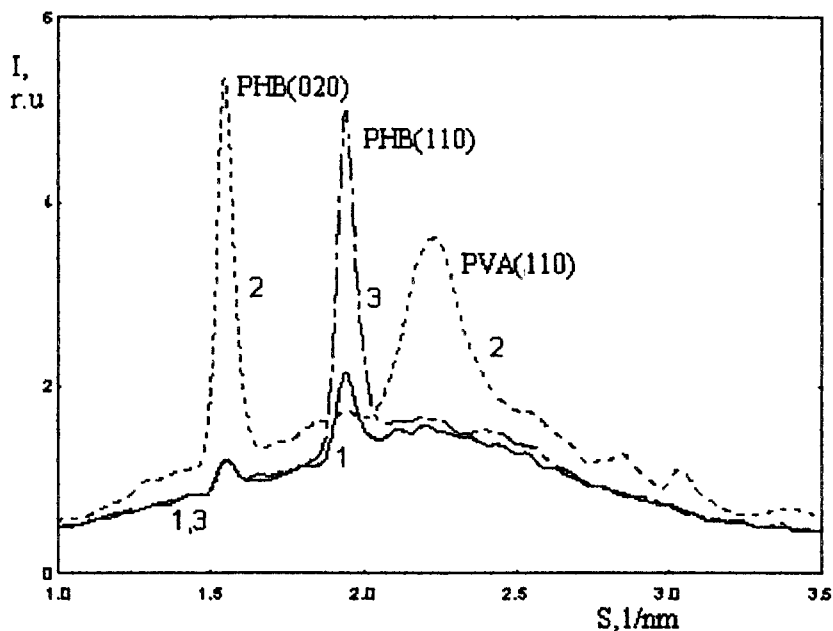
nated for PHB films.<sup>8</sup> The relative humidity in the feed compartment was maintained constantly at 90%. The water content in the registration compartment was very close to zero. The amount of water transferred through polymer films was determined by the weighting of KOH as an absorber of water. The deviation of five parallel measurements for each experimental point was averaged as 0.85%. The sensing device was accurate to  $\pm 0.0001$  g at 23°C.

## RESULTS AND DISCUSSION

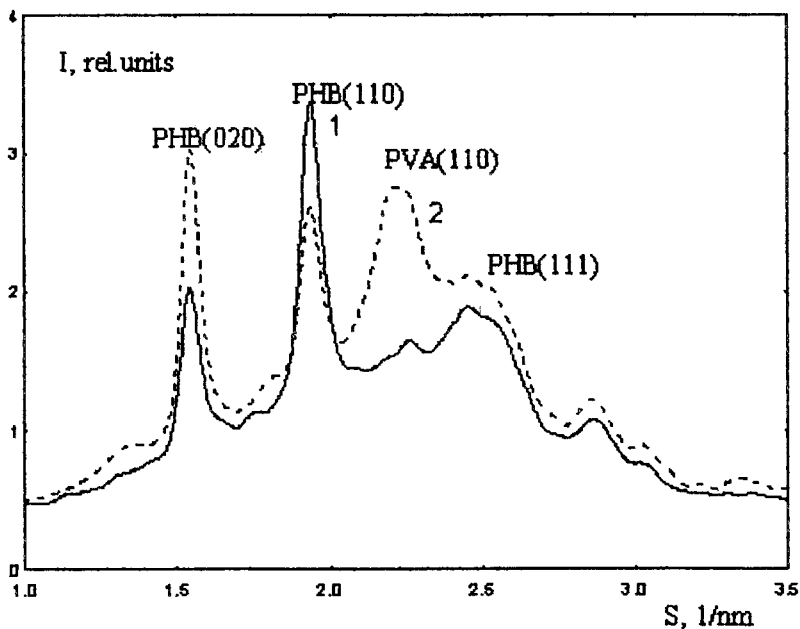
The results of DSC scans for PHB–PVA blends and the parent polymers which were prepared by extrusion are given in Table I. The low-temperature transition between 24 and 54°C may be related to the glass transition temperatures ( $T_g$ ) for both parent polymers (for PHB, 24.1°C, and PVA, 53.9°C) and polymer segments of these polymers interacting in the blends (see ref. 9). This perceptible shift of  $T_g$  can reflect a tendency for the miscibility of the components. The thermophysical characteristic analysis will be presented in detail in our forthcoming article.<sup>10</sup>

Along with the thermophysical data and the transparency in PHB–PVA films observed at a 0–30% concentration interval, the findings of the X-ray (WAXS) method show that each of the components is capable of forming its own crystalline phase. Analysis of the diffractograms (Fig. 1) allows extracting, in the general spectra, the reflexes which pertain to individual crystalline phases of PHB and PVA simultaneously. At all proportions of the components in the blends, PHB conserves the elementary cell parameters  $a = 0.576$  nm,  $b = 1.32$  nm, and  $c = 0.596$  nm, which correspond to the orthorhombic elementary cell.<sup>11</sup> The PVA reflexes are typical for quasicrystalline modification (the gamma form) constructed by parallel-oriented macromolecules in dense packaging.<sup>12</sup> In the diffractogram in Figure 1, the reflex at  $S = 2.21$  nm<sup>-1</sup> corresponds to the PVA phase.

WAXS measurements were taken at different orientations of the film position relative to the X-ray irradiation beam (Fig. 2). For all samples, the diffractograms reveal the existence of an axial cylindrical texture in PVA. The axis of the texture coincides with the extrusion direction and, hence, the PVA molecules in the quasicrystalline fields were oriented along the extrusion direction. In samples with 10 and 20% wt of PHB, a well-defined axial texture of PHB crystallites is evidence that the texture axis coincides with the direction of extrusion as well. However, the PHB crystallites are oriented relative to the texture axes so that the extrusion direction is in line with the axes  $a$  of the elementary crystalline cell. Hence, the axes of the PHB



**Figure 1** WAXS diffraction patterns for extruded film prepared from PHB–PVA blend at 20% wt PHB. Measurements were provided (1) along the extrusion direction, (2) normally to the extrusion direction, and (3) at a 20° angle relative to the extrusion direction. To 30% of PHB in the blends, the X-ray pattern shows evidence of a *cylindrical texture* in PHB.



**Figure 2** WAXS diffraction patterns for extruded film prepared from PHB-PVA blend at 30% wt PHB. Measurements were provided (1) along the extrusion direction and (2) normally to the extrusion direction. At this concentration, the crystalline structure of PHB in the blend is *isotropic*.

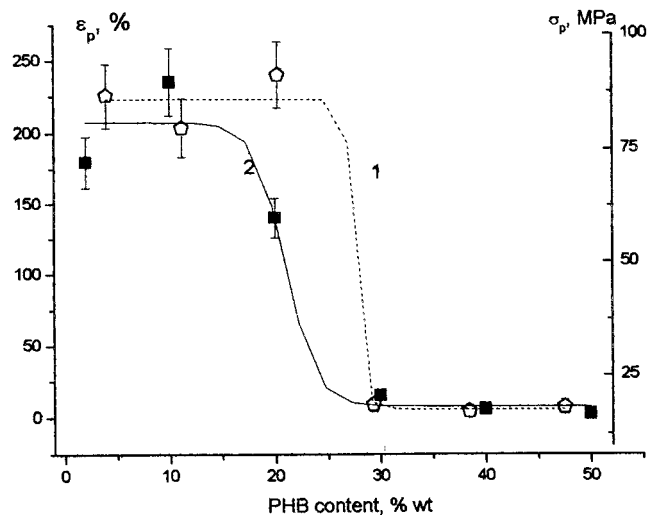
molecules are normally oriented relative to the extrusion direction.

The diffractograms of the samples containing 30 and 50% wt of PHB show that most of the crystalline phase in PHB is isotropic, without texture, and only a residual amount of oriented and textured crystallites is present in the 30% wt PHB-contained sample.

These findings allow the conclusion that, in the PHB-PVA blends at 30% wt PHB content, the structural transition from a textured to an isotropic crystalline state occurs. Such a transition could be attributed to phase inversion of the polymer matrix taking place in the same concentration range, about 30% wt of PHB. It is common knowledge that, in the range of phase inversion, both the crystalline and physical properties of polymer blends are changed (see, e.g., ref. <sup>13</sup>). In this work, we studied the effect of the structural inversion on the mechanical behavior of the blends at different concentrations of PHB. A drastic decrease was observed on curve (1) of the tensile strength-concentration and on curve (2) of the elongation at break-concentration (Fig. 3) in the same concentration interval. Besides, on the curve reflecting the dependence of the elastic modulus on the PHB concentration, there is a minimum located in the same concentration interval near 30% wt where the phase inversion proceeds, as shown in Figure 4. The following increase of the blend modulus reflects an increase of the concentration of structural elements (e.g., crystallites of PHB) which are responsible for the high-modulus behavior of the blend matrix as a whole system. At low PHB concentrations in the blends, their

behavior at rupture is preferably determined by the mechanical properties of PVA, while at the PHB concentration more than 30% wt, these characteristics are closely analogous to the behavior of the PHB matrix. The results presented in Figures 3 and 4 do not contradict the physical concept of phase inversion involving both crystalline fields and intercrystalline (amorphous) fields in the blends.

The transformation of the amorphous fields impacts upon important characteristics such as the permeability and diffusivity of water. The transport processes



**Figure 3** Mechanical characteristics of PHB-PVA blends at different concentrations of PHB. (1) Tensile strength; (○)  $\sigma_p$ ; (2) elongation at break; (■)  $\epsilon_p$ .

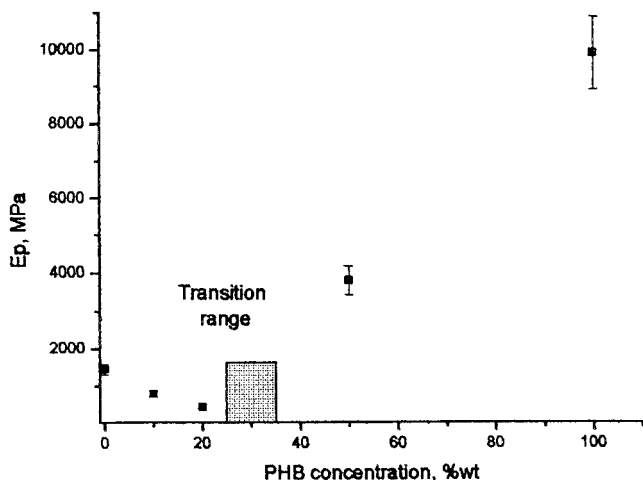


Figure 4 Effect of PHB concentration in the PHB-PVA blends on modulus of tension.

proceed exclusively in the amorphous part of any blend matrix and, hence, this process will be structure-sensitive relative to the change of structural organization in the intercrystalline fields. Kinetic curves of water-vapor permeation through the blend films at different ratios of PHB/PVA are presented in Figure 5. Contrary to permeability through the parent PVA films, all permeability curves through the blends have three specific ranges corresponding to three different ways of water diffusion.

The initial range (I, see Fig. 5) features a low rate of water permeation, where diffusion is conjugated with the immobilization of water molecules on functional groups of PHB (ester groups)<sup>14</sup> and more intensively on hydroxyl groups of PVA.<sup>15</sup> In this temporal interval of time, a transitional flux of water takes place that

is typical for all hydrophilic polymers. The next intermediate range (II) determines the quasi-steady-state regime of transport, where water diffusion is complicated by residual structural relaxation more typical for PHB molecules. An increase in water-vapor permeation is dictated by both increase of the free-volume ratio and segmental mobility in the blends. The last two effects result from screening the functional groups by the absorbed water molecules<sup>16</sup> as well as redistribution of hydrogen bonds in the blends as a response to the water effect.<sup>17</sup> The rupture of hydrogen bonds formed initially between ester (PHB) and hydroxyl (PVA) or between two hydroxyl groups as effective crosslinks promotes swelling in the blends and, as a consequence, an increase of both water diffusivity and water equilibrium sorption. The third range of permeability curves can be recognized due to the inflection point observed for all samples containing PHB. It seems likely that, to this moment, structural relaxation is completed and water transport proceeds in accordance with the regular diffusion mechanism.<sup>18</sup>

Increasing the PVA ratio increases the hydroxyl group concentration in the blends. An increase of the total hydrophilicity in the blend films determines a monotonic increase in equilibrium water sorption without visible point inflections or extrema (see Fig. 6). In spite of a possible transformation of the structure on crystalline and supermolecular levels, which was revealed by WAXS and the mechanical testing above, the equilibrium sorption of water molecules is sensitive only to the molecular structure. The amount of water molecules sorbed in the blends is determined by the nature and concentration of the functional groups. On the other hand, with an increase of the PHB content, the hydroxyl concentration in polymer systems is

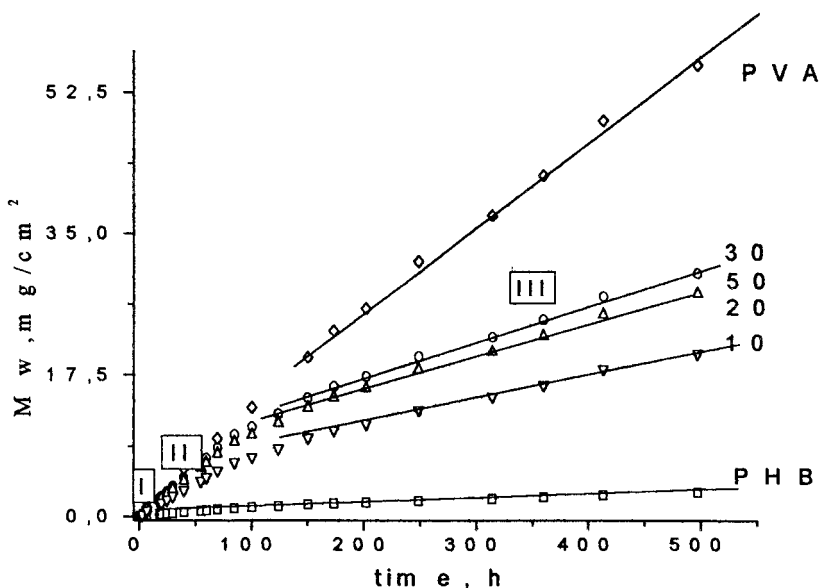


Figure 5 Kinetic curves of water permeability into films containing different ratios of PHB/PVA.

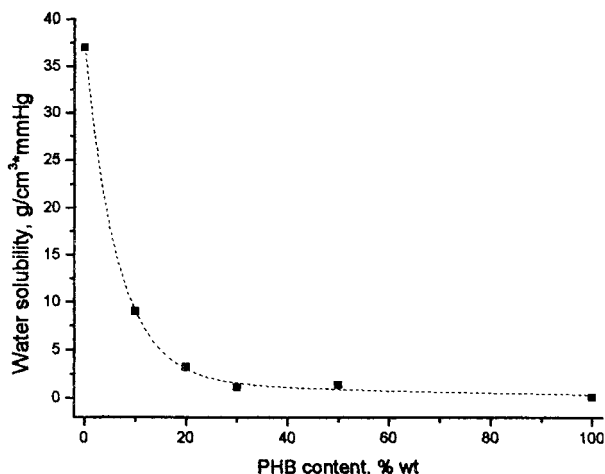


Figure 6 Water equilibrium sorption in the blends with different PHB concentrations.

decreased, that is, the replacement of the hydroxyl groups with the ester groups of PHB. So, the groups possessed by PVA with a high affinity to water molecules are replaced with ester groups of moderate affinity.

The permeability of water vapor as function of the PHB content has a maximum at about 40% wt of PHB, as can be seen in Figure 7. Probably, in this range, which is very close to the 30% range of phase inversion described above, the structure and morphology of the blends have the maximal amount of defects. In the range covered, 10–30% PHB, the deviation from the additive relation of water permeability is clearly observed. Even the first portion of the PHB blended with PVA in the ratio of 1:9 drastically depresses the water permeability, which could attest to the partial interaction of the components at an interval below 30% of

PHB. Most likely, the interaction occurs between the components in an amorphous state, whereas the crystalline fractions of both components form their own fields when the PHB and PVA crystallites do not influence each other. As follows from the above results, at the inversion point, the PVA crystallites did not change their textured organization, whereas the morphology of PHB was transformed from a cylindrical to an isotropic state (Figs. 1 and 2). The structural disorder in the isotropic matrix of PHB was observed in our works recently by WAXS, FTIR spectroscopy, and quartz-microbalance sorption methods.<sup>19–21</sup> Besides, we cannot exclude the leakage of water flux through defect zones formed on the border between two components, as it occurred in the PHB–polyethylene of low density (PELD) blends described in our work.<sup>22</sup> The sharp buildup of heterogeneity in the PHB–PVA blend films in a 30–50% wt interval lets one assume an intricate mechanism of water transport including both the proper diffusion and the transport through porous areas formed of structural elements of the blended components. In this situation, we have to treat these coefficients only as effective transport coefficients.

CONCLUSIONS

A blend design on the basis of polymer components with essentially different hydrophilicities is of academic and industrial interest, primarily for the control of such critical but little known characteristics as water permeability, equilibrium sorption, and diffusional mobility. The greater the difference between the polarity of the blended macromolecules, the harder it is to achieve a scantily miscible blends’ production. It is worth pointing out that, with the retention of mechanical properties, as has been shown for a PHB–PELD

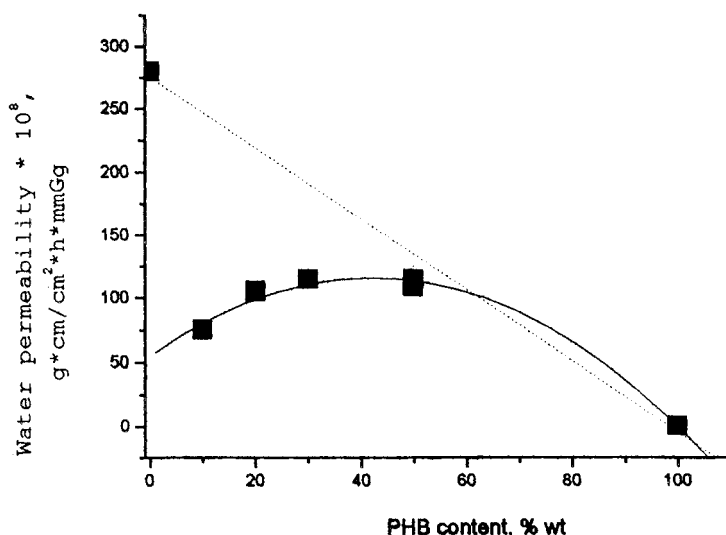


Figure 7 Water permeability through the films on the basis of PHB–PVA blends at 20°C. Dashed line describes the additive relation between water permeability and PHB content.

reinforced blend,<sup>22</sup> the heterogeneity or the microphase separation promote the achievement of chemically corrosive degradation and biodegradation or bioerosion. It is on morphological and transport levels that the control of the service properties for novel biodegradable polymer blends can be realized.

In spite of the 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 friendly environmental and biocompatible PHB could be treated as new generation of environmentally protected materials in the packaging industry, for agricultural application, as well as in biomedicine areas.

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