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Hydrophilicity Impact upon Physical Properties of the Environmentally Friendly Poly(3-hydroxybutyrate) Blends: Modification Via Blending

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Summary: We have integrated scientific research of polymer blends on the base of poly-3-hydroxybutyrate (PHB and its copolymers) with bench testing in blend preparation by both solvent casting and melt extrusion. As a second component, we have used traditional synthetic macromolecules with various hydrophilicity degree and hence with different morphologies and physical behavior. Besides, variation of polymer hydrophilicity permits to control both the service characteristic and the rate of (bio)degradation operating in the presence of water. Therefore, a substantial part of our work is devoted to water transport in the parent PHB and its blends. Combining the morphology knowledge (SEM, WAXS, FTIR tecynique), transport characteristics (permeability cells and McBain spring microbalance), and mechanical testing, we propose that blending of the parent biodegradable polymer with synthetic macromolecules is a perspective tool to design novel materials with improved characteristics. Both the water transport coefficients and the mechanical characteristics are essentially sensitive to structure and morphology of the blends. Hydrophilicity variation in the order LDPE $<$ SPEU $<$ PVA at blending with PHB shows that the morphology transformation in immicsible or partly miscible blends shifted along the PHB concentration scale as LDPE (at $\sim$16 wt% PHB) $<$ PVA ($\sim$30 wt% PHB) $<$ SPEU ($\sim$50 wt% PHB) Our instrumental monitoring the structural hierarchy of parent polymers and their blends as well as , simultaneously, the study of transport processes, their modeling, and computer simulating open up the way to understanding the precepts of polymer operation in corrosive and bioactive media.

Keywords: blending; crystallinity; mechanical properties; morphology; permeability; poly(3-hydroxybutyrate); synthetic polymers; water diffusion

Introduction

In the last view decades, bacterial poly(3-hydroxybutyrate) [**PHB**] and related poly-(hydroxyalkanoate)s [**PHA**s] attract much attention as biocompatible and friendly environmental materials with potential applications in medicine, packaging, agriculture at al.[1]. In contrast to synthetic polymers, PHAs including PHB have the essential advantages of being renewable resources without the use of hydrocarbon fossils. Besides, this class of polymers are biodegradable i.e. PHAs can be completely digested and metabolized by a wide variety of bacteria and fungi in living systems, soil and other aqueous media [2].

On the contrary to wide-spread biodegradable materials such as the starch-based plastics, polylactides and the others, PHAs show an advantageous combination in physical and exploitation characteristics. A challenging compromise of biomedical and transport properties for PHAs is complicated by the poor mechanical behavior

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(in particular, high brittleness) as well as the high cost yet. For addressing the above two problems : a) depressing in PHB (PHA) prices, b) improvement of mechanical behavior, we propose the specific blending of PHB and the abundant synthetic polymers containing different concentration of hydrophilic groups (diverse hydrophilicity) such as *hydrophobic* PELD, *hydrophilic* polyvinylalcohol (PVA) as well as *moderately hydrophilic* segmented polyetherurethanes (SPEU).

A preparation of the blends gives often rise to morphology heterogeneity of their matrices especially for immiscible or partly miscible polymer systems [3]. A multiphase structure organization, in itself, promotes the degradation rate due to the increase of both effective transport coefficients and functional group accessibility for (bio)corrosive agents. Such transport characteristics as permeability, diffusivity and sorption capacity [4] of bioactive/corrosive permeates (water, drugs, electrolytes at al.) determine not only service behavior of blends but the blend resistance against the environmental effect. The water barrier behavior of semi crystalline immiscible polymeric blends forming the disperse systems can be highly dependent on the chemical structure (hydrophilicity) and morphology of each component. This is especially true if the parent components differ themselves in water diffusion coefficients significantly.

Experimental

The powdered PHB were produced in Laboratory Biochemistry of Nitrogen Fixation of in accordance with State Standard of RF (TU 9393-001-0269944) Bach's Institute of Biochemistry and Biomer Co (Krailing, Germany) PHB Lot M-0997. Its chemical structure and crystallinity degree (70%) were determined earlier, molecular weight (M_η equal $4.1\ 10^5$ and $2.5\ 10^5$ respectively) was measured by intrinsic viscosimetry in chloroform solution; density is 1.27 g/cm^3. The granulated LDPE are commercial products of SAFCT (RF) designated standard (15803-020) with following characteristics: $M_\eta = 2.5\ 10^5$ and specific density 0.92 g/cm^3. The granulated SPEU was provided by NPO PolymerSynthesis (Vladimir, RF). It was based on poly(propylene glycol) with molecular weight 2100 as soft segment blocks. The hard segment blocks consisted of a 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol as the spacer. The weight ratio of hard blocks is 30 wt.%. The study is concerned with PVA 8/27 Russian trade mark. The residual acetate group concentration and Na acetate salt concentration in PVA comprise 8.2 and 0.04% wt. respectively. Averaged molecular weight (Mw) of PVA is 64 000 g/mol. with melting point equals 146 °C.

All preliminary mixed compositions with different ratio of parent components were loaded in a single-screw extruder (ARP-20). Temperature in a heater head did not exceed 185 °C and the frequency of the screw rotation was 100 min^{-1}. Drawing ratio (5.0) has controlled the production of the blend films with 40–50 μm thickness. The unblended parent components (LDPE, PVA and PHB) were also processes under identical extrusion conditions to undergo a thermal history similar to the history for the blends. . The SPEU granules and powered PHB were pressed between steel plates with polyimide film between the sample and the metal. The electric-heated plates of compression cell enables to control the temperature of the samples at 178 °C. Compression-molded films obtained from PHB-SPEU blends have the thicknesses in the range between 60 and 80 μm.

Diffusivities and water sorption isotherms were obtained using vacuum quartz spring microbalance technique at 25 °C, water permeability was estimated in a special two-compartment cell. Wide/small angle x-ray scattering curves were measured by X-ray diffractometer equipped by a computer controlled linear position sensitive detector designed in the Joint Institute of Nuclear Research (Dubna, Russia). Spectral characteristics, dichroism and H-D exchange data were obtained with

FTIR procedure (IFS-48 Brucker IR spectrometer). The tensile modulus and elongation at break of the films were determined from measurements on the Instron 1122 tensile apparatus.

PHB Blending with Hydrophobic LDPE

The thermograms of melting for PHB/LDPE blend with different compositions of the parent polymers show that during initial heating, the thermal curves of the blends have two peaks located in high-temperature (denoted by subscript 1) and low-temperature (subscript 2) ranges. Both peaks were found to belong to the individual components PHB and LDPE respectively and reflect melting points of these polymers in blends. Broad melting peaks at high-temperature after blending indicate the rise in the width of the crystalline size distribution for PHB. In Table 1, the thermal parameters of blends with different ratios of components as well as the parent components are summarized. As seen, the positions of the melting temperatures for the blends of any composition, T_{m1} and T_{m2}, are stable and close to the characteristics of the parent polymers. Hence, the crystalline areas of PHB and LDPE do not virtually affect the thermal properties of each other. Besides, the crystallization temperature of LDPE remains the same in the blends of various compositions. This is the circumstantial evidence of the stability of crystal structure parameters of LDPE after blending that has been confirmed by independent experiments on X-ray diffraction. The parameters of crystalline LDPE and PHB phases with axial texture are known to be stable [5]. A decrease in the crystallinity degree observed for both components in the blends is rather determined by segmental interaction in amorphous areas and by low rates of structural relaxation in the system studied.

The water flux through the blend barriers is significantly affected by the morphology of the component that composes the continuous phase [6]. Scanning electron micrographs of PHB/LDPE blends, obtained recently [7], have shown that the continuous medium is formed preferably by LDPE. Besides, that is very important, the geometry, distribution as well as orientation of dispersed component, PHB, influence the transport in the blends. The total water permeability of the blends (P_W) can be described by the following equation:

$$P_W = \alpha_S^{PE} F_{PE} P_W^{PE} + \alpha_S^{PHB} F_{PHB} P_W^{PHB} + \alpha_S^{Int} P_W^{Int} \quad (1)$$

where P_W^{PE}, P_W^{PHB}, and P_W^{Int} are the water permeabilities in phases of LDPE, PHB, and through the interphase respectively; α_S^{PE}, α_S^{PHB}, and α_S^{int} are the fractions of the film cross section of each component and interphase; F_{PE} and F_{PHB} are function characterizing the effect of polymeric segments' orientation on the water permeability in phases of LDPE and PHB respectively.

$$\alpha_S^{int} = 1 - \alpha_S^{PE} - \alpha_S^{PHB} \quad (2)$$

Table 1.
Thermophysical characteristics of both PHB/LDPE blends and the parent polymers.

PHB/LDPE ratio, %: % wt.	T_{m1}, °C.	T_{m2}, °C.	T_{cr2}, °C.	ΔH_1, J/g	ΔH_2, J/g	X_1, %	X_2, %
0:100	—	107.0	89.6	—	70	—	40
2:98	172.0	106.4	89.8	58	58	42	35
4:96	172.6	106.3	89.4	48	55	45	29
8:82	171.8	106.5	89.5	34	60	47	30
16:84	173.2	106.8	89.7	40	60	49	28
32:68	173.2	106.9	89.5	48	35	55	25
100:0	175.4	—	—	61.9	—	69	—

T_{m1} - position of high-temperature peak; T_{m2}, - position of low-temperature peak; T_{cr2} - crystallization temperature of LDPE; ΔH_1 - melting enthalpy in high-temperature range, ΔH_2 - melting enthalpy in low-temperature range; X_1, X_2 - crystallinity degree for each component (DSC data).

According with our scanning electron microscopy data [7], the porous structure in the interphase is formed and, hence, parameter P_W^{Int} can be treated as hydraulic permeability that includes both the water diffusion and viscous flow of liquid [8]. In Fig. 1 the 3-dimensional mapping of water permeability through the LDPE/PHB blend films (J_W) is demonstrated. The content of PHB varied in range from 0 to 32% wt. The anomalous transport featured by a maximum on the 'permeation rate – time' curves is much more pronounced for blends with high concentrations of PHB but is unavailable for the parent (LDPE) film. The anomaly is most likely to be caused by structural relaxation in the LDPE/PHB interphase.

At low concentration of PHB (2–4 %wt) the blend resistance to water flux (reciprocal permeability) is maximal and exceeds the initial resistance of the parent LDPE (Fig. 2A). At the higher content of PHB the reciprocal permeability monotonically decreased and, in the limit, reached the value of parent PHB. The excessive values of the water barrier characteristic respecting the parent polymers could be related with perfect orientation of dispersed PHB. This biopolymer is arranged in the blend matrix as fibrils which are well oriented normally to flux direction [7]. It is significant that the same manners have both the dichroism ratio (Fig. 2B) and mechanical tensile strength (here not shown) dependence on the PHB concentration. It is apparent from the above data that transport behavior of water in the blended films is substantially affected by the orientation of polymer segments (F_i) in LDPE continuum phase and by the defects/pores formed in interphase areas (α_S^{Int}, P_W^{Int} in Eq. 1) if one suggests that tensile strength was dominantly determined by defects of the heterogeneous matrix of two immiscible polymers.

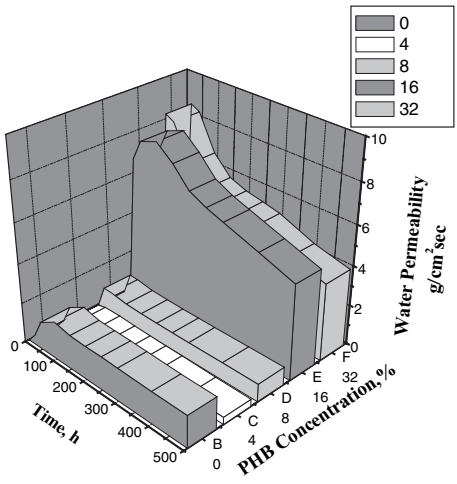

Figure 1.
3-D mapping for PHB-LDPE blend films (water permeability $\times 10^9$-PHB content- time of contact). Content of PHB in the blends: 0, 2, 4, 16, 32 wt%.

PHB Blending with Hydrophilic PVA

The results of DSC scans for PHB/PVA blends and the parent polymers at various proportions of the components are given in Table 2. The low-temperature transition between 24 and 54 °C may be related to the glass transition temperatures (Tg) of both parent polymers (for PHB is 24.1 °C and PVA is 53.9 °C) and polymer segments of these polymers interacting in blends, see [9]. This perceptible shift of Tg may reflect the tendency for miscibility of the components. The other thermophysical characteristics were presented in a preliminary paper [10].

Along with thermophysical data and the light transparency of PHB-PVA films observed at 0–30% concentration interval, the X-ray (WAXS) results show that each of the components is capable of forming its own crystalline phase. Analysis of diffractograms (Fig. 3) enables to extract in general spectra the reflections that correspond to individual crystalline phases of PHB or PVA. At all proportions of the components in the blends, PHB keeps the elementary cell parameters $a = 0.576$ nm, $b = 1{,}32$ nm, and $c = 0.596$ nm which correspond to orthorhombic elementary cell [11]. The PVA reflections correspond to quasi crystalline modification (the gamma-form) due to parallel-oriented macromolecules in dense packaging [12].

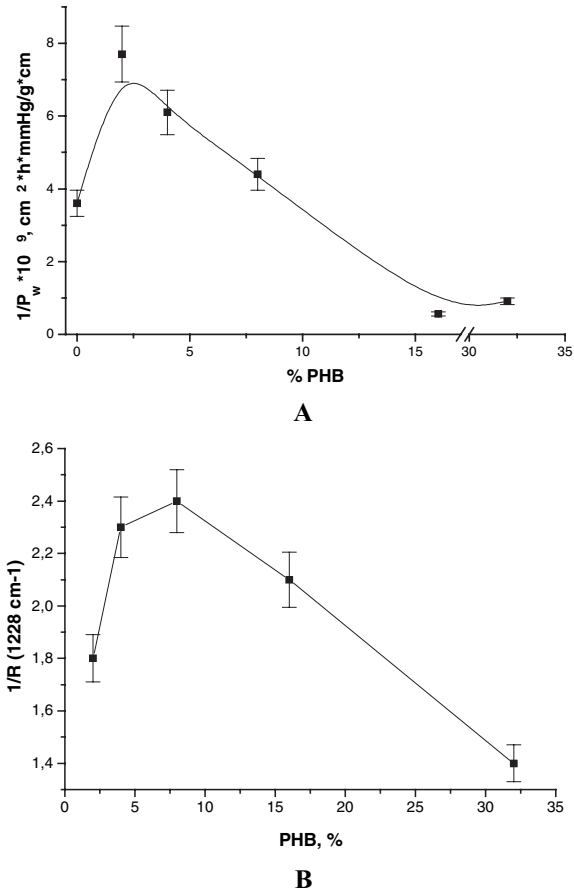

Figure 2.
Comparison of reciprocal permeability of water (A), FTIR dichroism (B) as function of the PHB content in PHB-LDPE films.

In Fig. 3 the reflex at $S = 2.21\ nm^{-1}$ corresponds to the pure PVA phase.

WAXS measurements were taken at the different orientations of film positions relative to X-ray irradiation beam. For all samples the diffractograms reveal the existence of axial cylindrical texture in PVA. The axis of texture coincides with extrusion direction and hence the PVA molecules in quasicrystalline fields oriented along extrusion direction. In samples with 10 and 20% wt of PHB (Fig. 3a) a well-defined axial texture of PHB crystallites shows that the texture axis coincides with direction of extrusion. However, the PHB crystallites oriented relative to the texture axes so that the extrusion direction was in line with the axe ''a'' of elementary crystalline cell. Hence, the axes of PHB molecules are normally oriented relative to extrusion direction. Diffractograms of the samples containing 30 and 50%wt of PHB show that the most part of crystalline phase in PHB is isotropic, without texture, (Fig. 3b) and only residual amount of oriented and textured crystallites is present in 30%wt- PHB-contained sample.

Table 2.
Glass transition temperatures of blends with different content of PHB.

PHB Content, %wt	0	10	20	30	50	100
Tg, °C	53.9	32.7	28.5	25.3	25.9	24.1

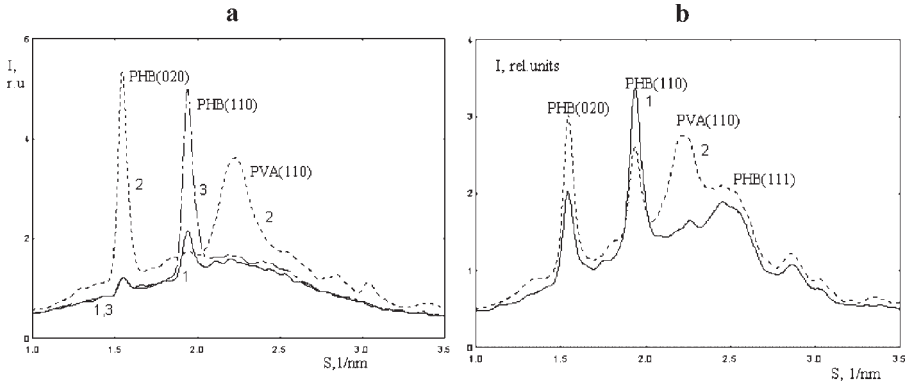

Figure 3.
X-ray (WAXS) patterns of PHB-PVA blends. 3a – concentration of PHB is 10 wt%, 3b – concentration of PHB is 30 wt%.

These findings allow to conclude that in the PHB/PVA blends at 30%wt PHB content the structural transition from textured to isotropic crystalline state occurs. Such transition could be attributed to phase inversion of 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 morphology and physical properties of polymer blends are changed. The transformation of the amorphous fields has to affect such important characteristics as permeability and diffusivity of water. The transport processes proceed exclusively in amorphous part of any blend matrix and hence this process will be structure-sensitive relative to change of structural organization in inter crystalline fields.

Increasing the PVA ratio increases actually the hydroxyl group concentration in the blends. A rise of total hydrophilicity in the blend films determines a monotonic increase in equilibrium water sorption without visible point inflections or extremums . In spite of possible transformation of structure at crystalline and super molecular levels, that was revealed by WAXS and mechanical testing, the equilibrium sorption of water molecules is sensitive to the molecular structure only.

Amount of water molecules sorbed in the blends is determined by nature and concentration of the functional groups. On the other hand, with a rise of PHB content the hydroxyl concentration in polymer systems is decreased due to the replacement of the hydroxyl groups by ester groups of PHB. So the groups possessed by PVA with high affinity to water molecules are replaced with the ester groups of moderate affinity.

The permeability of water vapor as function of PHB content has a maximum at about 40%wt of PHB as shown in Fig. 4. Probably, in this range that is very closed to 30% range of phase inversion described above, the structure and morphology of blends have the maximal amount of defects. In the range covered 10–30% PHB, the deviation from additive relation of water permeability is clearly observed. Even the first portion of PHB blended with PVA in ratio 1:9 depresses drastically the water permeability that could attest the partial interaction of the components at interval beneath 30% of PHB. Most likely, the interaction occurs between the components in amorphous state, whereas the crystalline fractions of both components form the own fields when the PHB and PVA crystallites do not influence each other. As it follows from above results, at inversion point the PVA crystallites did not change their textured organization whereas morphology of PHB has transformed from cylindrically anisotropic to isotropic state (see Figs. 3a and 3b).

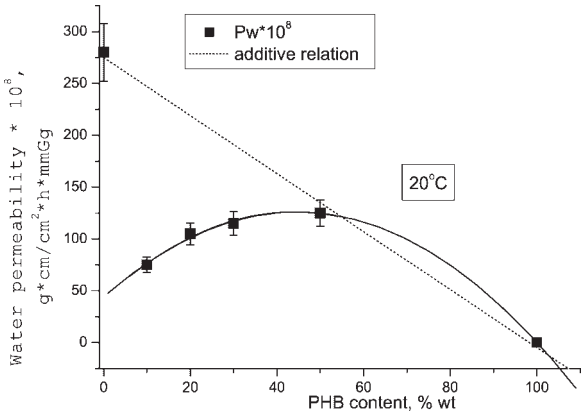

Figure 4.
Dependence of water permeability on ratio of polymer components in PHB-PVA blends.

It is worth noting that permeability as polymer characteristic is a complicated characteristic including both water solubility and diffusivity (the proper mobility of water molecules). Therefore, it is a great deal to reveal the effect of blend composition on water diffusion coefficients. In Fig. 5, the diffusion coefficients presented as function of PHB content in the PHB-PVA blends. To emphasis the correlation between mechanical and diffusion characteristics we report the tensile strength data in this same figure.

The inflection points are clearly observed for both curves and the positions of these points coincide with the phase inversion points revealed above. As in case of mechanical behavior (Fig. 5), at low PHB concentrations the diffusion characteristics of the blends are preferably determined by diffusion coefficients of PVA, while the diffusion behavior after 30%PHB point exceeds essentially the diffusion in parent polymer, PHB.

Comparing the water diffusivity in PHB ($Dw = 1^{*}10^{-8}$ cm^2/s [5]) with diffusivity in blends at the maximal concentration of PHB (50%), we notice that difference between these characteristics amounts to as much as a power of values. As in case of permeability analysis we may explain this difference in diffusivities due to structural

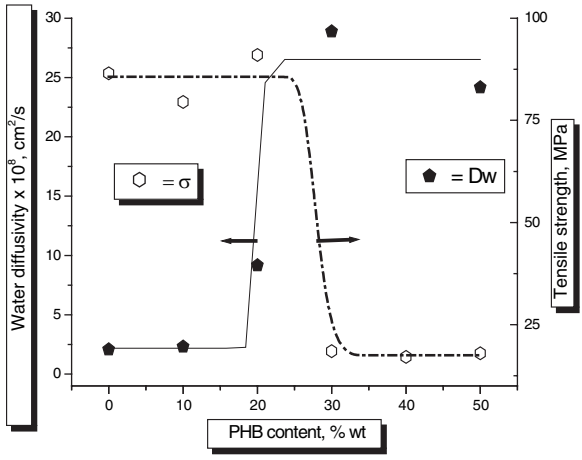

Figure 5.
Water diffusivity (1) and tensile strength (2) of PHB-PVA blends as functions of PHB concentration.

imperfection. Structural disorder in isotropic matrix of PHB has been observed in our works recently by WAXS, FTIR spectroscopy and quartz – microbalance sorption methods [13].

Besides, we can not exclude the leakage of water flux through defect zones formed on the border between two components just as it happened in PHB/LDPE blends described in our work [7]. The sharp build-up of heterogeneity in PHB/PVA blend films in the concentration range between 30 and 50 wt% indicates a 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 has to treat these coefficients preferably as effective transport characteristics.

Moderately Hydrophilic Blends: PHB-SPEU Compositions

Transport coefficients rank among the most important characteristics of polymeric items being used in therapy and surgery as well as for the design of controlled release systems. Special position in medical material area is assigned to segmented polyether(or ester) urethanes (SPEU) due to their optimal combination between biocompatibility and mechanical behavior [14]. With the intent to improve SPEU biocompatibility over the parent characteristic as well as for the design of the novel matrices for drug delivery we proposed the PHB-SPEU blends with different content of PHB.

We emphasize that the water diffusion coefficients in each of two parent polymers are very similar. At room temperature they differ as few as 2.5 ($Dw = 2.4 \cdot 10^{-8}$ cm^2/s in SPEU and $Dw = 0.95 \cdot 10^{-8}$ cm^2/s in PHB). Because of this, the variation of PHB content gives hardly the drastic method of blend diffusivity regulation. Whereas the water blend permeability (as the product of diffusivity by solubility) could be remarkably varied by changing the PHB content as a consequence of the difference between the water solubilities in PHB (1 wt%) and SPEU (5.8 wt%). Besides, the dependence of water permeability on the blend content has a maximum value similar to PHB-PVA systems (as in Fig. 5). This maximum is located near the point 50:50 wt% on the PHB:SPEU concentration scale. At this concentration ratio, the special points on the curves : 1) tensile strength – PHB concentration (maximum) and 2) elongation at rupture – PHB concentration (inflection point) are approximately located as it can see in Fig. 6. Most probably the

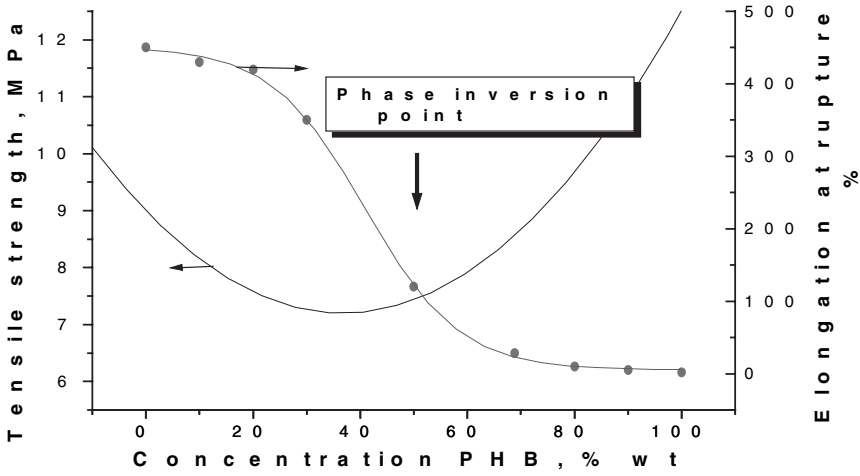

Figure 6.
Mechanical properties (tensile strength – 1, elongation at rupture – 2) at different concentrations of PHB in PHB-SPEU blends.

structural transfer (the phase inversion) occurs just where the ratio of concentrations in the blends achieves the value 1:1.

Conclusion

Summarizing, it should be noted that both the water transport coefficients and the mechanical characteristics are essentially sensitive to primary structure (hydrophilicity) and morphology of polymer blends. Variation of polymer hydrophilicity in the following order LDPE < SPEU < PVA at blending with PHB enables to point out that the morphology transformation in immicsible or partly miscible blends shifted along the PHB concentration scale as hydrophobic LDPE (after ~16wt% PHB) < PVA (at ~30 wt% PHB) < SPEU (at ~50 wt% PHB). Diffusion coefficients and permeation reflect the morphology changes and simultaneously correlate with mechanical behavior of the blends. These results combined with transport characteristics will be sufficient to enable a justified view on transport mechanism in multiphase-forming polymers for medicine, biotechnology, membrane separation processes, constructional materials etc, when each polymer couple is compatible with the environment.

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