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CHARACTERIZATION OF THE STRUCTURE AND PROPERTIES FOR THE POLYMER BLENDS BASED ON POLY-3-HYDROXYBUTYRATE AND POLYISOBUTYLENE

Keywords: polyisobutylene, poly(3-hydroxybutyrate), blends, morphology, rheology, DSC, degradation, weight loss, soil.

Design of bioerodible composites combining synthetic and natural polymers is an important stage for development in constructional and packaging materials which are friendly environmental ones during exploitation and thrown on a garbage dump. For this object the composites on the base of poly(3-hydroxybutyrate) (PHB) and polyisobutylene (PIB) were prepared in plunger extruder. Morphology of the blends was studied by AFM (NTegra Prima) with cantilever NSG-01 with frequency 0,5-1,0 Hz and DSC (DSC-60 9Shimadzu, Japan). Rheology characteristics were obtained by plastometer Stress Tech (Rheologica Instruments, Sweden). Degradation was performed in soil at 22-25°C with following weighing to determine weight loss.

Two-phase matrices of the composites show displacement of glass transition temperatures of individual phases. Comparison of experimental and theoretical values of viscosity confirmed the formation of a continuous matrix with less viscous PHB. This greatly simplifies the processing of melts of compositions PHB-PIB. Microbial degradation of PHB phase occurs almost entirely within 100-125 days. The remaining friable matrix PIB is much more susceptible to degradation by other destructive factors (oxygen of the air, temperature, mechanical stress). Process of biodegradation of PHB phase influences on the structure of PIB. This is reflected in a sharp decrease of average molecular weight of PIB.

Ключевые слова: полиизобутилен, поли(3-гидроксibuтират), смеси, морфология, реология, ДСК, разложение, потеря массы, почва.

Разработка биоразлагаемых композитов, сочетающих синтетические и природные полимеры, является важным этапом развития конструкционных и упаковочных материалов, безвредных для окружающей среды в процессе эксплуатации и утилизации. Для этого были приготовлены композиты на основе поли(3-гидроксibuтирата) (ПГБ) и полиизобутилена (ПИБ) в плунжерном экструдере. Морфология смесей изучалась с помощью АФМ (NTegra Prima) с консолью NSG-01 с частотой 0,5-1,0 Гц и ДСК (DSC-60 9Shimadzu, Япония). Реологические характеристики были получены на пластометре Stress Tech (Rheologica Instruments, Швеция). Дегградацию проводили в почве при 22-25°C с последующим взвешиванием для определения потери массы. Двухфазные матрицы композитов показывают смещение температур стеклования отдельных фаз. Сравнение экспериментальных и теоретических значений вязкости подтвердили образование непрерывной матрицы с менее вязким ПГБ. Это значительно упрощает обработку расплава композиций ПГБ-ПИБ. Микробная дегградация ПГБ фазы происходит почти полностью в пределах 100-125 дней. Остаточная рыхлая матрица ПИБ гораздо более восприимчива к дегградации под воздействием других деструктивных факторов (кислорода воздуха, температуры, механических напряжений). Процесс биодегградации фазы ПГБ влияет на структуру ПИБ. Это приводит к резкому снижению средней молекулярной массы ПИБ.

Introduction

One of the most pressing problems facing humanity is increasing pollution. In this regard, question of recycling of synthetic polymeric materials arises very sharply. Plastics production rates are growing exponentially and production volumes hundreds of millions of tons annually. One of the most dynamic areas of the use of plastics is packaging industry (40 to 50% of the total production of plastics). Thus, billions of tons of municipal solid waste products constitute more than half of the short-term or one-time application on the basis of large common polyolefins. A possible solution of this problem is to create biodegradable polymer compositions. The fastest growing trend in this area is the use of polyhydroxyalkanoates (PHAs). Some physical and chemical characteristics of PHA are similar to these of synthetic polymers (polypropylene, polyethylene). However, in addition to their thermoplasticity, representatives of PHAs have optical activity, increase induction period of oxidation, exhibit the piezoelectric effect and, what is most important, they are characterized as being biodegradable and biocompatible. At the same time, the PHAs have

disadvantages (high cost, brittleness) which can be partially or completely compensated by using composite materials based on blends with other polymers, with dispersed fillers or plasticizers. Taking into account all the above, we have suggested to create a mixed polymer composite based on poly-3-hydroxybutyrate (PHB) and polyisobutylene (PIB).

Objects and methods

The objects of the study were high molecular weight PIB of mark «P-200» and PHB Lot 16F. The poly-3-hydroxybutyrate was obtained by microbiological synthesis in company «BIOMER®» (Germany). PHB is a white fine powder; the density is 1.25 g/cm³; the molecular weight is 325 kDa. Polyisobutylene of high molecular weight «P-200» is a white elastic material, transparent in thin films, odorless, with density of 0.93 g/cm³ and with molecular weight of about 175-225 kDa.

These materials have been chosen due to their economic expediency and the valuable combination of physical and chemical, physical and mechanical and other properties of individual polymers - PHB is a

brittle thermoplastic; PIB - an elastomer. Preparation of composite materials based on combinations of plastics and elastomers is well known: plastics are used as polymeric fillers in elastomers, improving their technological and working characteristics; elastomers effectively improve strike viscosity and reduce brittleness in compositions based on plastics.

The polymer compositions were prepared in the following proportions: PHB:PIB = 10:90, 20:80, 30:70, 40:60, 50:50 and 60:40 (by weight ratio here and hereinafter). Then, the individual polymers were investigated. The first stage of blending was carried out on laboratory mixing rolls with the roll length of 320 mm and diameter of 160 mm. Temperature of the back roll was 60°C, temperature of the front roll was 50°C. In these conditions the compositions were obtained, in which the micropowder of PHB was distributed in the continuous matrix of PIB. Deeper joining, mutual segmental solubility of polymers require an additional high temperature treatment of compositions, so the second stage of the composition processing was carried out in plunger extruder at the temperature of 185°C.

Average molecular weight of the elastomer was characterized by viscometry method. Average molecular weight of PIB was calculated according to the equation Mark-Houwink:

$$[\eta] = K \times Mm^\alpha, \quad (1)$$

$[\eta]$ – the intrinsic viscosity, ml/g; Mm – average molecular weight of the polymer; K, α – constants for a given system "polymer-solvent".

Heptane was used as solvent, the constants - $K=1,58 \times 10^{-4}$, $\alpha=0,69$ [8]. For each sample, a series of solutions were prepared with different concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 g/100 ml), and then determines the relative, specific and intrinsic viscosity. The calculated molecular weights presented in Table 1.

Investigation of the structure of the compositions by atomic force microscopy was performed on the tunnel atomic force microscope brands Ntegra Prima (company «NT-MDT») (cantilever NSG-01 with a frequency of 0.5-1 Hz). Investigations were carried out by semicontact mode. Microtome cuts were made on the brand Microm HM-525 (company «Thermoscientific», Germany).

Investigation of the structure of the compositions was carried out by differential scanning calorimetry on differential scanning calorimeter DSC-60 (company «Shimadzu», Japan). Samples of PHB-PIB blends weighing several mg were placed in open aluminum crucibles with a diameter of 5.8 mm and a height of 1.5 mm and weighing 13 mg upper temperature limit of 600 °C. Temperature range - from minus 100 to plus 250 °C, heating rate of 10 °/min. Liquid nitrogen is used to generate low temperature. Instrument calibration was performed according to indium, tin and lead.

The rheological curves of pure polymer melts and their mixtures were obtained with the multifunction rheometer «StressTech» (company «REOLOGICA Instruments AB», Sweden). The measuring cell consisted of two parallel planes (the lower plane was fixed, the upper plane being a rotating rotor); the shear

rate was 0.1 s^{-1} , the temperature range was 443-513K (170-240°C). The lower limit of the temperature range was chosen by the melting temperature of PHB (174.4°C – the data obtained for DSC), the upper limit is the beginning of irreversible degradation in polymers.

Polymer samples were subjected to soil degradation in a laboratory at a temperature 22-25°C. Samples in the form of a film thickness of 50 microns was placed in the soil to a depth of 1.5 - 2 cm. Biodegradation rate was assessed by evaluating the mass loss of the samples. Mass loss was fixed by weighing the samples on an analytical balance.

Results and Discussion

Properties of mixed polymer compositions are determined by many factors, among which in the first place should be allocated phase structure (ratio and the size of the phase domains). Therefore at the first stage of the research attention has been paid to study the structure of formed compositions. In the investigation of samples with a low content of PHB (10 - 30% by weight) has been found that it forms a discontinuous phase i.e. distributed in a continuous matrix PIB as separate inclusions of the order of 1-2 microns. The results of atomic force microscopy for the composition ratio of PHB-PIB 20:80 shown in Figure 1.

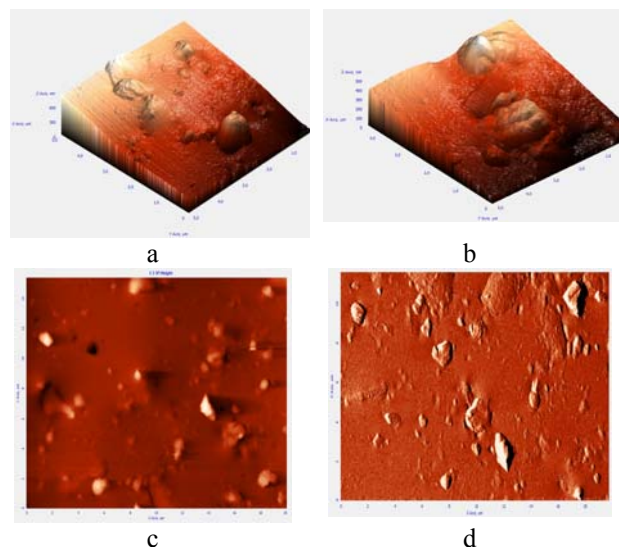


Fig. 1 - Photomicrographs of the relief of films with PHB-PIB ratio of 20:80 (scan size 5×5 μm) (a, b) and AFM phase contrast image of the film with a ratio of 20:80 PHB-PIB (scan size 20×20 μm) (c, d)

Atomic force microscopy is considered one of the most perspective methods for studying polymer blends is because this method allows to clearly define the phase boundary and its scale. Polymer identification was performed by controlling the interaction of the probe with the sample surface at different points. When approaching the surface of the cantilever is deflected downward (to the sample) due to attractive forces until the probe comes into contact with the sample. When the probe is withdrawn from the studied surface, a hysteresis is observed, associated with the adhesive forces. Adhesion forces between the probe and the

sample are forcing them to remain in contact, which causes the cantilever to bend. Phase of the polymers were very clearly identified by mapping curves "approach-removal" of the probe.

Probable range of the phase inversion is an important characteristic for mixed biodegradable composites. This allows from a practical point of view to establish the minimum concentration of PHB (at which a continuous phase is formed) for intensive biodegradation as microorganisms must be able to penetrate deep into the mixed composite. When compared with the atomic force microscopy of samples with different proportions of the components was found that in investigated materials continuous matrix formation occurs when PHB content in the mixture of about 40-50% by weight. The results of atomic force microscopy for the composition ratio of PHB-PIB 50:50 shown in Figure 2.

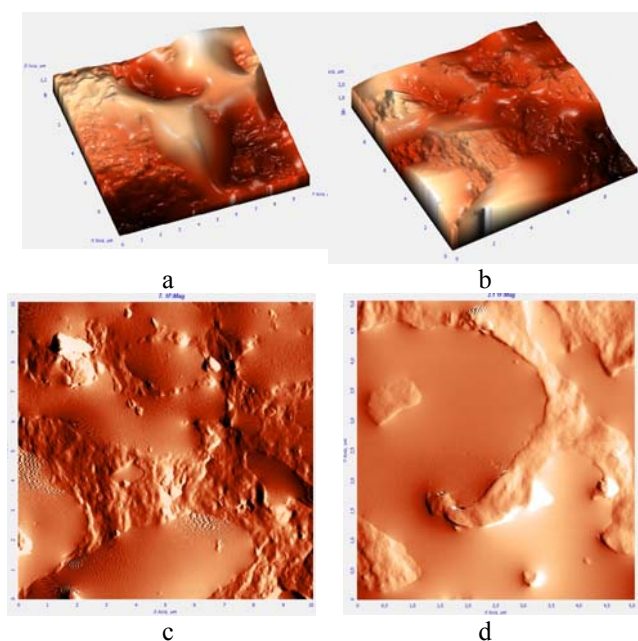


Fig. 2 - Photomicrographs of the relief of films with PHB-PIB ratio of 50:50 (scan size 10×10 μm) (a, b) and AFM phase contrast image of the film with a ratio of 50:50 PHB-PIB (scan size 10×10 μm) (c) and 5×5 μm) (d)

Thus, by atomic force microscopy were determined scale structures and distributions of polymers according to the ratio of the starting components in the mixture, and the approximate range of probable phase inversion (about 40-50% by weight of PHB).

Determination of the glass transition temperature is an informative method of research the phase structure of polymer blends. In the case of mixed compositions glass transition may occur in each phase separately, if polymers do not interact with each other. In another case glass transition in mixtures is fully cooperative process, involving macromolecules mixed polymer segments. This composition would have single glass transition temperature which varies monotonically depending on the mixture composition [1]. The glass transition temperatures of polymer components of the

mixtures were determined by differential scanning calorimetry. The results of DSC are shown in Figure 3.

In all cases, the specific heat jump was recorded, which corresponds to the glass transition of phases polymers. It was noted displacement values of glass transition temperature of phase PIB to higher temperatures with increasing content of PHB (from -68°C for pure PIB to -64°C for the composition with 60% by weight of the PHB). For PHB phase displacement of values of glass transition temperature is shown in Figure 4.

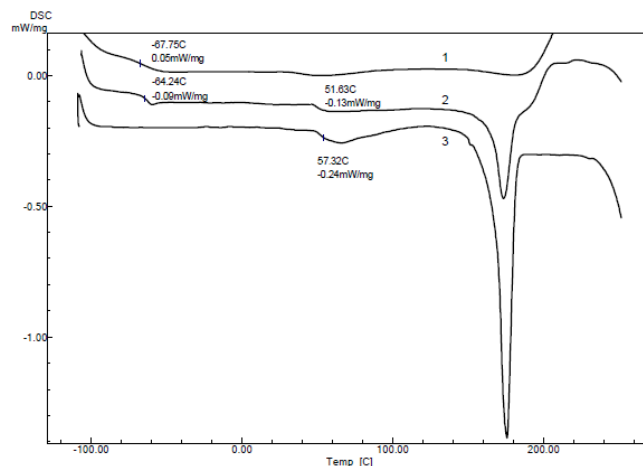


Fig. 3 - DSC curves of the samples (1 - pure PIB, 2 - 20% PHB, 3 - pure PHB)

As can be seen from the data presented, the displacement of values of glass transition temperature of PHB occurs about 6 - 7 °C. Most often in the literature as reasons for this phenomenon is called a limited solubility of the mixture components in each other (from a fraction of a few percent) [1-3]. However, for the polymers probability such variant is extremely small because of the significant thermodynamic incompatibility. More probable reasons of displacement of the glass transition temperature may be changes of the supramolecular structure of polymers when mixing; as well as differences in thermal expansion coefficients of polymers in the region above and below the glass transition temperature.

The glass transition temperature change deserves attention because is a sharp jump in the of PHB content of 50-60% by weight. This phenomenon may also be due to the probable phase inversion (previously established by microscopy methods) at said ratio of the components. Continuous structure more rigid of PHB has a higher glass transition temperature than the individual inclusions of thermoplastic material, isolated from each other by a continuous matrix of PIB. Thus, as a result of studies on the structure of compositions of PHB-PIB was confirmed formation of heterogeneous two-phase systems. For biodegradable polymer compositions it may be advantage, because this system is more susceptible to external influences destructive.

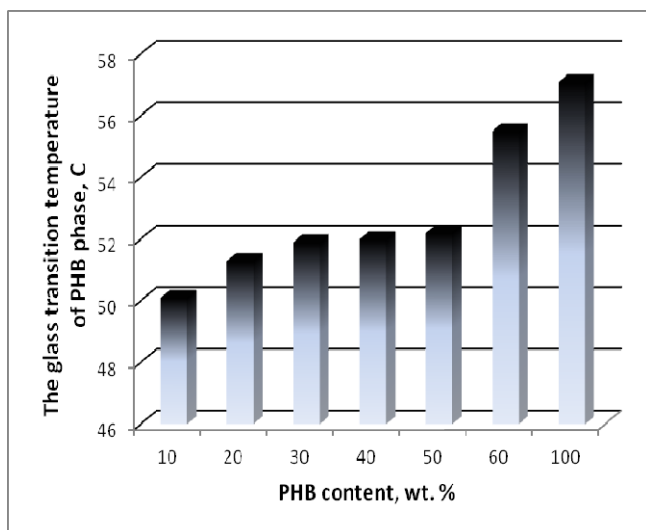


Fig. 4 - Changes in the glass transition temperature of phase PHB

However, for practical use of PHB-PIB compositions is necessary to evaluate the possibility of processing these materials into finished products. As most polymer blends are processed by melting them, investigations of rheological properties of these compositions are of great scientific and practical interest. Information about the structure of composition that can be obtained on the basis of rheological investigation is the level of intermolecular interactions, the degree of macromolecules ordering, the phase structure of polymer blends. Dependence «melt viscosity – temperature» were investigated for all compositions. The viscosity values at various temperatures for blends of polymers with different ratios are shown in Figure 5.

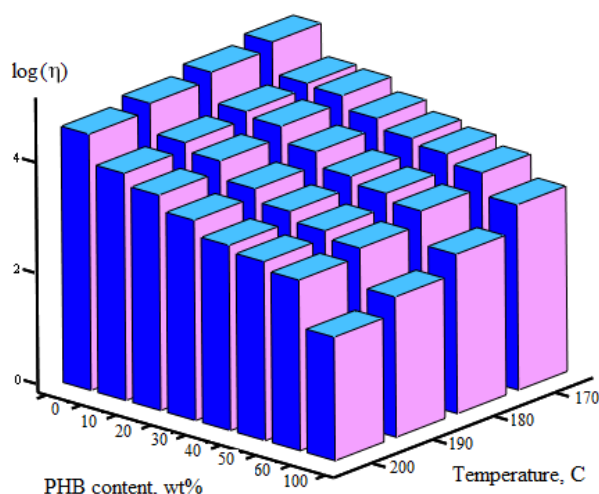


Fig. 5 - The viscosity values at various temperatures for blends of polymers with different ratios

The viscosity values of the composition decreases considerably with increasing temperature and increasing the content of PHB that gives the chance regulation of technological properties of compositions in a wide range. Based on the significant difference of the solubility parameters calculated previously [6], it

seems reasonable assumption on the formation of a biphasic system melts of mixtures of these polymers. The assumption of formation of two-phase mixtures of melts of these polymers seems justified based on significant difference in the solubility parameters which calculated previously [6]. Kerner-Takayanagi equation applicable to describe the rheological properties of two-phase mixtures of polymers [1]:

$$\eta = \eta_m \cdot \frac{(7 - 5v_m) \cdot \eta_m + (8 - 10v_m) \cdot \eta_f - (7 - 5v_m) \cdot (\eta_m - \eta_f) \cdot \varphi_f}{(7 - 5v_m) \cdot \eta_m + (8 - 10v_m) \cdot \eta_f - (8 - 10v_m) \cdot (\eta_m - \eta_f) \cdot \varphi_f} \quad (2)$$

η – viscosity of the mixture, Pa × s; η_m – viscosity of the matrix, Pa × s; η_f – viscosity of the dispersed phase, Pa × s; φ_f – volume fraction of the dispersed phase; v_m – Poisson's ratio of the matrix (assumed equal to 0.5).

This expression describes the dependence of the properties of the mixture composition, excluding inevitable phase inversion in the mixture. According to (2) the viscosity of the blend composition is graphically expressed by the two curves corresponding to the two limiting cases when one or the other phase is continuous throughout the range of compositions of the polymer mixture. Theoretical values of the viscosity of the compositions of various compositions were calculated based on the viscosity base polymers. Calculations on model of Kerner-Takayanagi at different temperatures are shown in Figure 6.

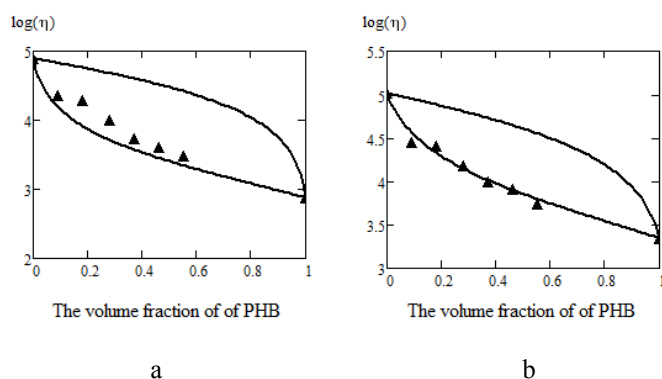


Fig. 6 - Viscosity of the composition at a temperature of 180 °C (a) and 170 °C (b) (- theoretical calculations on model of Kerner-Takayanagi; ▲ - experimental data)

By analyzing data of Figure 6, it was found that PHB forms a continuous matrix in the molten polymer at any ratio. The experimental values of the viscosity are close to the bottom theoretical curve, which corresponds to the calculation for the case of the formation of the matrix of PHB. Thus, during the melting of PHB observed phase inversion phenomenon - in accordance with the laws of [4, 6] more fluid melt PHB forms a continuous phase in the entire range of concentrations. Basic rheological parameters of polymer blends determined by the properties of the polymer matrix, so the properties of melts are generally defined by PHB. Lower viscosity of the melt blend composition (due to the formation of a continuous matrix PHB) in this case will significantly simplify the processing of the

investigated materials. Also, the data in Figure 6 are consistent with the position that the greater the difference in viscosity of mixed polymers, the earlier the formation of a continuous matrix less viscous component.

Previous studies [7] revealed that the main physical and mechanical characteristics (tensile strength, tensile modulus, elongation at break) PHB-PIB composition containing 30-50% by weight of PHB, not inferior to traditional polymers used in the production of packaging (polyethylene of different brands). But the undeniable advantage of the compositions PHB-PIB is the possibility of biodegradation. It has been found that mixtures containing 40-60% PHB stepwise lose mass when exposed to soil. In the first stage (100 days) intensive degradation of phase PHB occurs under the action of microorganisms. The results of the first stage of this scenario are PIB samples with very high surface area. In the second step (after 100 days), mass loss is stabilized and is much slower.

Table 1 - The average molecular weight of PIB samples

PIB samples	The intrinsic viscosity	The average molecular weight
The original sample	0,68	185 000
The sample after 200 days of exposure in the soil (0% PHB)	0,65	175 000
The sample after 200 days of exposure in the soil (60% PHB)	0,49	115 000

As can be seen from Table 1, the average molecular weight PIB sample (previously containing PHB) much less compared to the original molecular weight PIB and PIB after exposure to soil. Significant impact of PHB phase on the ability of PIB to degradation in soil was found by research of the molecular weight of the elastomer. Destruction of the original structure PIB can occur due to physical factors (large specific surface films), chemical factors (interaction of the products of biodegradation of PHB with PIB phase, and initiation of the degradation of the elastomer) and biological factors (accumulation of microorganisms biomass on the surface of mixed films and therefore some microorganisms can use the matrix PIB as a carbonaceous substrate for growth.

Conclusions

There are some conclusions drawn in the course of studying structure and properties of polymer system «PHB-PIB»:

1. Structure of mixed compositions of PHB-PIB investigated by atomic force microscopy; confirmed the formation of a heterogeneous two-phase structure. PHB forms a continuous elongated structure in the matrix of PIB when content of PHB in the mixture is greater than 30%.

2. Displacement of glass transition temperatures of individual phases in a mixture of polymers determined by differential scanning calorimetry. This may be indicative of their limited interaction, despite the significant difference of the solubility parameters.

3. Comparison of experimental and theoretical values of viscosity confirmed the formation of a continuous matrix less viscous PHB. This greatly simplifies the processing of melts of compositions PHB-PIB.

4. Microbial degradation of PHB phase occurs almost entirely within 100-125 days. The remaining friable matrix PIB is much more susceptible to degradation by other destructive factors (oxygen of the air, temperature, mechanical stress).

5. Process of biodegradation of PHB phase influences on the structure of PIB. This is reflected in a sharp decrease of average molecular weight of PIB.

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