Biopolymer Geotextiles Based on Mixtures of Polyhydroxybutyrate and Polylactic Acid

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Abstract. In this work, studies of the hydrolytic destruction of biodegradable nonwoven fibrous and film materials based on the mixtures of biobased polymers - polyhydroxybutyrate and polylactic acid, have been carried out. Fibers were obtained from a solution in chloroform by electrospinning. It was shown that materials with high content of polylactide had a low resistance to hydrolysis as compared to polyhydroxybutyrate. Nonwoven fibrous materials obtained by electrospinning had a higher water absorption and a high reactivity to hydrolysis, which significantly accelerated (by about 5 times) the biodegradation process under environmental conditions. The degree of hydrolytic destruction of fibrous materials based on polylactide and mixtures with its content of 50 wt.% or more is higher than that of samples enriched with polyhydroxybutyrate. The studied materials can be successfully used as nonwoven geotextiles for reinforcing the soil on the slopes of various types of roads being capable of accelerating the germination of grass cover.

1. Introduction
Developing environmentally friendly completely biodegradable film and fibrous materials for medicine, hygiene, environmental protection (eco-sorbents), soil reinforcing on the slopes during road construction (geotextiles), etc. is an urgent task today \cite{1,2}. Geosynthetic materials for road construction are currently made on the basis of polymers (polyethylene, polyamide, polypropylene, etc.). Their main functions are the following: filtration, water drainage, prevention of soil erosion (geomats, geocells). The material slows down the soil erosion and deformation due to climatic action. Protection of the slopes surface is a common problem in building most road, hydraulic, and railway construction projects. Slopes are exposed to constant destructive effects, so all the slopes are eroded by precipitation, the slopes of dams are affected by the flow of water, waves, and ice, as well as the slopes of railway embankments are exposed to constantly dynamic loads. Under the influence of such a number of loads, the slopes are quickly damaged and the body of the embankment (or structure) begins to deform, and these processes occur very quickly. One of the key factors for reinforcing the slopes is their rapid overgrowth with grass cover. To accelerate plant growth on the porous geotextiles, meshes or mats, non-woven fibrous
biopolymer coatings can be used, which stimulate and accelerate plant germination and rooting [3]. By combining hydrophobic and hydrophilic natural biopolymers, it is possible to regulate the transport of water through the geotextile structure [4-6]. In addition, porous coatings based on natural polymer materials significantly accelerate the growth and rooting of herbal plantations [7].

Ultrathin nonwoven fibrous materials based on polyesters synthesized from naturally occurring monomers, for example, polylactic acid (PLA) and bacterial biopolymer poly(3-hydroxybutyrate) (PHB), are usually obtained by electrospinning from solutions or melts [8,9]. These fibers fulfill the above two criteria, and therefore can be used as fine biodegradable coatings. In the process of electrospinning, ultra-thin fibers form 3D-structures in the form of fibrillary membranes (mats) with high and gradient porosity and large specific surface area. The high water permeability and absorption selectivity of these membranes in relation to organic weakly polar substances create good prospects for their use in the road construction. An additional important advantage of the proposed systems in comparison with traditional polymer absorbents based on polyolefins, polyfluorides, polyamides, and others is the ability of PLA and PHB to biodegrade after the end of their service life, which makes their use environmentally friendly [10].

In the process of biodegradation of such materials, hydrolytic destruction is an important factor [11-13]. The purpose of this work was to study the effect of an aqueous medium on the material structure for predicting the biodegradation of nonwoven fibrous polymeric materials based on hydrophobic PHB and moderately hydrophilic PLA.

2. Experimental part

Poly-(3-hydroxybutyrate) (PHB) supplied by BIOMER (Germany) with a viscosity-average molecular weight of $4.6 \times 10^5$ g/mol and polylactic acid (PLA) of the brand NatureWorks Ingeo™ 3801X Injection Grade PLA supplied by SONGHAN Plastics Technology Co. (USA) with a viscosity-average molecular weight of $1.9 \times 10^5$ g/mol are used for obtaining materials under investigation. The materials were obtained in the following ratios of PHB/PLA: 0:100, 10:90, 50:50, 70:30, 90:10, 100:0 wt.%. To prepare molding solutions, chloroform (CF) of the category "chemically pure" was used. Fibers were obtained by electrospinning according to the method described in [14]. The differential scanning calorimetry (DSC) analysis of the samples was carried out by a Netzsch DSC 204 F1 (Germany) in an inert argon atmosphere with a scanning rate of 10 K/min. The average fiber diameter was determined by scanning electron microscopy using a Hitachi TM-1000 scanning electron microscope (Japan). The study of the hydrolytic destruction of fibrous materials was carried out in a phosphate buffer, which simulated the effect of the physiological environment. To measure the hydrolytic degradation of the fibrous materials, they were incubated in 0.025M phosphate buffer solution (pH=7.4) at 70°C for 21 days. Then, the nonwoven fibrous materials were removed from the phosphate buffer at regular intervals and washed with distilled water, exposed in an incubator for 3 hours at a temperature of 70°C, and then weighed (the measurement error was 0.1 mg). In experiments with phosphate buffer, the buffer was changed every 3 days.

The biodegradation tests were carried out under soil composting conditions. During the experiment, soil moisture (60 %) and pH were maintained at a constant level. The samples of materials with an area of 4 cm$^2$ were placed in a chamber with soil for 45 and 70 days. After a predetermined exposure period, the samples were removed from the chamber, cleaned of soil, weighed and subjected by visual inspection. The parameters of the soil compost were the following: the nitrogen content of 300-550 mg/kg; the content of phosphorus oxides of 330-550 mg/kg; the content of potassium oxides of 450-850 mg/kg. At the end of the experiment, the change in the mass of the materials relative to the initial one was calculated using Eq. 1:

$$\Delta m = \frac{m_1 - m_2}{m_1} \cdot 100\%,$$ (1)
where $m_1$ is the mass of the initial sample before testing, $m_2$ is the mass of the sample after degradation in the soil.

3. Results and discussion

In this work, the moisture absorption of nonwoven fibrous materials based on PHB and PLA, which are cylindrical fibers with a diameter of 1-9 µm randomly stacked relative to each other, were studied. PHB and PLA differ in the degree of hydrophilicity and, accordingly, in the sorption capacity. In addition, PHB has a high degree of crystallinity (65-85%), while PLA is a glassy polymer, which also affects the value of sorption.

Calculations by the BET method showed that for nonwoven matrices of the studied compositions, the specific surface area was small and was equal to 0.6-0.9 m$^2$/g. According the obtained data, the nonwoven materials are matrices with a fairly dense fiber packing. Dense packing is explained by the presence of fibers of different diameters and geometries in the material. In this case, fibers of small diameters fill the free volume between fibers of large diameters. Thus, the filling of the free volume in the nonwoven material occurs, similar to the formation of superdense compositions of polymer composite materials with particles of different dispersion. Due to the high packing density, a relatively small sorption capacity of PHB/PLA nonwoven fibrous materials should be expected.

The non-equilibrium structure of the polymer fiber, as well as the difference in the sorption-diffusion properties in water, should affect the chemical resistance of the material when exposed to aggressive media [15-17]. Fig. 1 shows the kinetic dependences of the weight loss of non-woven fibrous materials of PHB after the exposure to phosphate buffer.

![Figure 1](image_url)

**Figure 1.** Dependence of the weight loss on the exposure time in the phosphate buffer of the samples of nonwoven materials PHB/PLA: 0:100 (curve 1), 10:90 (curve 2), 50:50 (curve 3), 70:30 (curve 4), 100:0 (curve 5), 90:10 (curve 6).

The fibrous materials with a high PLA content (50-100 wt.%) underwent intense hydrolytic degradation. The materials based on pure PHB after 21 days of the experiment lost up to 10 wt.% of their weight. The samples of PHB and PHB/PLA (with a PHB content of over 50 wt.%) had an induction period of up to 6 days. At the same time, the materials on the basis of pure PLA after 6 days of exposure lost about 40 wt.%. As shown above, PLA is more hydrophilic than PHB (the sorption capacity of PLA fibers is almost 3 times higher than PHB). In addition, the degree of crystallinity of the former, according
to DSC data, is approximately 2.5 times less than that of PHB. This leads to a comparatively rapid hydrolysis of PLA relative to PHB.

Fig. 2. shows the microphotographs of the fibrous materials based on pure PHB after exposure to phosphate buffer. The initial fibrous materials based on PHB, PLA and their mixtures were statistically stacked ultra-thin fibers. After 21 days in the phosphate-buffered saline, the samples were actively exposed to hydrolytic action, the fibers became brittle, and individual filaments disintegrated into fragments. At the same time, the degree of destruction of the material obtained from PLA and mixtures with PLA content more than 50 wt.% was higher than that of samples enriched with PHB.

![Figure 2. Microphotographs of the samples of the initial PHB fibrous material (a) and the same material after 21 days of exposure to phosphate-buffered saline (b).](image)

Figure 2. Microphotographs of the samples of the initial PHB fibrous material (a) and the same material after 21 days of exposure to phosphate-buffered saline (b).

The soil tests of the nonwoven fibrous material based on PHB was carried out [18]. In the literature, the processes of biodegradation of biopolymer materials under natural conditions are widely described [19-22]. Fig. 3 demonstrates photographs of samples of the nonwoven fibrous material based on pure PHB during exposure to soil. The sample after exposure for 45 days had separate focal traces of biodegradation, but retains its original integrity. After 70 days of exposure in soil (Fig. 3, c), the film sample lost its integrity, and its fragments had defects in the form of holes and shells.

![Figure 3. Photographs of the nonwoven material based on pure PHB after: 0 (a), 45 (b), and 70 (c) days of soil test.](image)

Figure 3. Photographs of the nonwoven material based on pure PHB after: 0 (a), 45 (b), and 70 (c) days of soil test.

The dependence of the weight loss of the samples on the period of exposure in the soil is given in Fig. 4. After 90 days of exposure to soil, nonwoven materials based on PHB almost completely
degraded. The rate of destruction of the nonwoven sample based on PHB was so high that within 45 days the sample completely disintegrated.

![Figure 4](image)

**Figure 4.** Dependence of the weight loss of the nonwoven fibrous material based on pure PHB on the exposure time in soil.

4. **Summary**

The nonwoven fibrous materials based on PHB/PLA blends obtained by electrospinning had a high water absorption and a high reactivity to hydrolysis, which significantly accelerates (by about 5 times) the biodegradation processes under environmental conditions. The degree of hydrolytic destruction of fibrous materials based on PLA and the mixtures with 50 wt.% or more PLA was higher than that of samples enriched with PHB. The fibrous nonwoven material based on PHB/PLA is very promising for developing biomaterials for geotextiles stimulating plant growth with a biodegradation period under environmental conditions of less than 3 months. The studied materials can be successfully used as the outer layer of geofabrics for reinforcing the soil on the slopes of various types of roads, capable of accelerating the germination of grass cover.

5. **References**

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