Impact of environmental factors on agrofibers based on “green” polymers

Yu V Tertyshnaya1,2, A A Olkhov1, N S Levina2, I A Bidey2, M N Moskovskiy2
1 Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygina str., Moscow, 119991, Russia
2 Federal Research Agro-Engineering Center VIM, 1st Institutsky proezd, 5, Moscow, 109428, Russia
E-mail: moraxella@bk.ru

Abstract. Influence of different environmental factors on the degradation of fibrous samples based on polylactic acid and poly-3-hydroxybuturate was studied in this work. The article presents data obtained by differential scanning calorimetry (DSC), scanning electron microscopy (SEM). The hydrolytic degradation of nonwoven fibers, degradation in soil and under UV light were investigated. It was found that the degree of degradation of the material obtained from the 5% PHB solution was higher than from 7 and 9 %. It was shown that after 60 days of soil exposure, the samples of nonwoven fibers PLA and PLA-PHB collapsed into fragments and melting temperature of both samples was reduced by 11-12 °C. The degree of crystallinity also significantly decreased.

Introduction

World consumption of polymers has increased exponentially since the nineteen fifties. According to numerous forecasts, the crude oil resources will become appreciably exhausted after 2050; therefore, the use of alternative materials will become inevitable. Already now the development and production of biodegradable “green” polymers of vegetable origin is a topical problem for many developed countries. Interest in natural polymers such as poly-3-hydroxybutyrates (PHB), polylactide (PLA), starch, chitin, cellulose, etc., increased in the past decade [1-3]. Items made of these polymers are safe for the environment and humans. Under the influence of ultraviolet, heat, air and soil microorganisms they degrade to low molecular compounds and easily assimilate in soil, being included in closed ecological circuit [4].

PLA is a biodegradable thermoplastic polyester derived from biomass such as sugar, corn, beet, which possesses excellent physical and mechanical properties combined with biocompatibility and biodegradability properties [5]. Due to its initial production costs, the starting applications of PLA have been focused on high value products such as medical devices [6]. Because of the high market demand of biodegradable based products in recent years, PLA based products are manufactured commercially in many countries. Their applications include film, food packaging, textiles, disposable bottle and tableware [7].

Another promising, biodegradable polymer, which will be the subject of this work, is poly-3-hydroxybutyrate. Poly-3-hydroxybutyrate (PHB), for example, is synthesized inside cells and is degraded to CO2 and water when disposed in biological systems [8]. The main advantage of PHBs
over other types of biodegradable polymers is its biodegradability under both aerobic and anaerobic conditions, such as buried in soil, immersed in activated sludge, and submerged in sea water. In recent years, studies of PLA combined with PHB have shown that the mechanical properties of the blend are intermediate between those of the individual components. Specifically, PLA-PHB blends exhibit greater flexibility and hydrolytic biodegradation than PLA or PHB alone [9].

Polymer-based nanoscale composites can be produced by different fabrication methods. In this work the fibrous materials of PLA-PHB were prepared by electrospinning. Electrospinning is one of the most prominently used techniques for producing micro- to nanometer fibers because it is a simple, cheap and versatile process.

Experimental
Preparation of Fibrous Material Poly(3-hydroxybutyrate) (Biomer, Germany) was used in the form of powder obtained by microbiological synthesis with a molecular mass of $2.5 \times 10^5$ g/mol, a melting point ($T_m$) of 175–180°C, and a density of 1.25 g/cm$^3$. To prepare the spinning solutions, chloroform of reagent grade was used. Polylactide (Nature works 4032D, USA) with a molecular mass of $1.9 \times 10^5$ g/mol and a melting point ($T_m$) of 163–165°C, and a density of 1.24 g/cm$^3$ was used. The fibers were obtained by electrospinning.

**DSC** The degree of crystallinity and melting temperature of the samples were studied with differential scanning calorimeter DSC 214 Polyma (Netzsch, Germany) at a heating rate of 10 K/min and a sample weight of 5±0.1 mg. The temperature scale was calibrated against an indium standard ($T_m = 156.6°C$, $\Delta H = 28.44 J/g$).

**Electron Microscopy** The average diameter of fibers was determined by electron microscopy using a Hitachi TM-1000 scanning electron microscope (Japan). A fiber sample was applied to a receiving cylinder with an electrically conductive scotch tape during fiber formation, and micrographs were taken at different degrees of magnification and solution flow rates. The fiber width was measured using the Photoshop.CS3.Extended program. At least 300 fibers were to be measured for constructing the size distribution and at least 100 fibers for determining the average diameter.

**UV Irradiation** To study the UV aging, fiber samples with a mass of ~50 mg were selected and placed in a chamber with a DRT-375 high-pressure mercury lamp, where they were kept to a state of brittle fracture. At certain time intervals (20–30 min), the samples were taken out and weighed on a Vibra AF-R220CE balance with an accuracy of 0.0001 g, and the mass loss was determined.

**Hydrolytic Degradation** The hydrolytic destruction of fibrous materials was studied in a phosphate buffer, which simulates the effect of a physiological medium. To measure the hydrolytic degradation of PHB fibrous materials, they were incubated in a 0.025 M phosphate buffer solution (pH 7.4) at 70°C for 21 days. The nonwoven fibrous materials were then taken out of the phosphate buffer at regular intervals, ashed with distilled water, placed in an incubator at 70°C for 3 h, and then weighed on a scale (the measurement error was 0.1 mg). In the experiments with the phosphate buffer, the buffer was replaced every 3 days.

**Degradation in soil** The microbial activity of soil was monitored with cotton along the extension of the experiment. The soil was maintained at approximately pH 7 and a relative humidity of 0.87 g water/g wet soil. Three specimens of each sample were extracted after certain times of burial in soil, cleaned and kept in a desiccator during 4 days in order to ensure water desorption before being analyzed.

Results and discussion
According to table 1, the crystal phase of PHB in the samples melts in a very narrow temperature range: 176–177°C. This means that the modification of PHB crystallites in the initial powder and fibers does not change. The initial temperature of decomposition ($T_{\text{inj}}$) and the temperature of the maximum of the decomposition peak ($T_{\text{max}}$) in the fibers are much lower than in original PHB (286°C); the difference is 11–14°C at the initial stage of thermal decomposition and 13–18°C when the maximum is reached on the thermogram of destruction.
Table 1. Thermophysical parameters of PHB samples.

| PHB content, wt % | $T_m$, °C | $\chi_c$, % | $T_{\text{init}}$, °C | $T_{\text{max}}$, °C |
|------------------|-----------|-------------|-----------------------|----------------------|
| 5                | 176.5     | 70          | 244                   | 273                  |
| 7                | 177       | 73          | 239                   | 270                  |
| 9                | 176       | 72          | 236                   | 268                  |

Let us first consider the effect of UV radiation. Figure 1 shows the kinetic dependences of mass loss by the PHB nonwoven fibrous materials on the time of exposure to UV radiation. According to figure 1, the intensity of the photooxidative destruction of the fibrous materials increases when the PHB concentration in the spinning solutions decreases. This occurs because fibers with a larger diameter are obtained at increased polymer concentrations in the spinning solution. As shown in [10], as the concentration of PHB increases during fiber formation, it undergoes more complete crystallization, and the amorphous region of the polymer phase becomes more compact, which, in turn, leads to increased fiber resistance to UV radiation.

![Figure 1](image)

**Figure 1.** Dependences of mass loss of the nonwoven fibrous samples obtained from the (1) 9, (2) 7, and (3) 5 wt % PHB spinning solutions on the UV irradiation time.

Thus, the fiber formation from more concentrated PHB solutions increases their resistance to photooxidative destruction. According to figure 1, in the fibers obtained from the 7 and 9% PHB solutions, even an induction period appears, which increases more than twofold when passing from 7 to 9% solution.

Similar results were obtained in our study of the hydrolytic effect on the nonwoven fibrous materials of the phosphate buffer solution as a model of the physiological environment of a living organism. Figure 2 presents the microphotographs of fibrous materials after exposure for 14 and 21 days. According to figure 2, after 14 days of buffer action, the materials retained their original morphology regardless of the polymer concentration in the spinning solution; after 21 days, the samples were actively hydrolyzed, and the fibers became brittle and broke into fragments. The degree of degradation of the material obtained from the 5% PHB solution was higher; as the sample had thinner fibers, less time was needed for interaction with the buffer and degradation.
In the second part of the work we present the results of studies of nonwoven fibers PLA and PLA-PHB with 10 wt % of PHB content. Fibrous material can be used as a covering, for example, for germination of breeding seeds. During the application of agrofiber inevitably gets into the soil, so the study of biodegradation in the soil of these materials is necessary. Biodegradation of polymers usually takes place in two main steps: primary degradation, in which fragmentation of the polymer chain occurs due to hydrolysis or another oxidative reaction, and ultimate biodegradation, in which the microorganisms assimilate the low M<sub>w</sub> chains formed. Both the PLA fibrous material and the PLA-PHB sample should be well degraded in the soil due to the combined action of moisture (hydrolysis) and microorganisms. Active biodestructors are fungi, which quickly affect polymeric materials based on natural polyesters [11]. The most aggressive micromycetes in relation to PLA and PHB are Aspergillus Niger, Penicillium Chrysogenum and Trichoderma Viride.

**Figure 2.** Micrographs of the samples fibrous material from the 5% solution (a), fibrous material from the 7% solution (b) and of the same samples after hydrolysis in a phosphate buffer solution: after 14 days of storage (c) and after 21 days of storage (d).

**Figure 3.** Photographs of the PLA-PHB sample after 60 days degradation in soil.
In our experiment, after 60 days of soil exposure, the samples of nonwoven fibers PLA and PLA-PHB lost about 30 wt.% and collapsed into fragments (figure 3). In figure 3 one can see the small fragments, pores and dirt, which is not removed and is the result of the action of microorganisms.

Thermophysical characteristics of the initial samples of non-woven material and after using them as agromaterials were determined by the method of DSC. The data are presented in the table 2.

| Sample      | $T_m$, °C | $\chi_c$, % |
|-------------|----------|-------------|
| initial     | after degradation | initial     | after degradation |
| PLA         | 164      | 152         | 40           | 25           |
| PLA-PHB     | 163/171  | 150/–       | 39/56        | 23/–         |

It is noticeable that during the experiment the samples of nonwoven fibers undergo changes in the structure. The melting temperature of both samples is reduced by 11-12 °C, there is a significant decrease in the degree of crystallinity. Moreover, for the PLA-PHB sample, the change in the PLA $\chi_c$ value is 16%, and the melting peak of PHB is generally absent, which indicates the fracture of the crystal structure and the processes of degradation.

Conclusion
Biopolymer nanofibers of PHB, PLA and PLA-PHB were produced by electrospinning considering different solution types. Based on the experimental data with PHB fibers, we can conclude that the polymer concentration in the spinning solution is one of the main factors responsible for the formation of the molecular and supramolecular structure of nonwoven fibrous materials by electrospinning.

Fibers with a content of 5 wt % PHB in solution are subjected to hydrolytic destruction in the buffer and UV radiation more quickly. The study of nonwoven agrofibers (PLA and PLA-PHB) showed that biodegradation in the soil is quite intense, which is confirmed by the DSC data.

It follows from the foregoing that fibers with varied structural organization and resistance to aggressive environmental factors can be obtained depending on the requirements to the material.

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