Nonwoven polylactide fibers: properties and application

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Abstract. Non-woven argofibers based on polylactic acid and poly-3-hydroxybuturate was obtained by electrospinning. An experiment on growing winter wheat (Triticum aestivum L.) on non-woven polymer substrates was carried out. High seeding qualities of wheat seeds are shown both in the control sample and on the fibers. It is determined that the mass of the plant, the length of the roots is greater in plants sprouted on non-woven fibers PLA and PLA-PHB. During the growth and development of plants, the resulting non-woven materials undergo biodegradation. Thermophysical parameters of nonwoven agrofibers were determined by differential scanning calorimetry.

1. Introduction
The search for innovative technologies is one of the urgent tasks facing modern agricultural production of cereals and vegetables. One of ways of environmentally friendly production is sowing of seeds on excipient located in the soil made of nonwoven fibers biodegradable polymers [1]. Fibrous material can be used also as a covering, for example, for germination of breeding seeds.

Nonwoven materials from poly-3-hydroxybutyrate and polylactide solutions were obtained by electrospinning. Electrospinning is a complex process involving the hydrodynamics of weakly conducting Newtonian liquids and phase transformations – evaporation of the solvent and removal of the polymer fiber [2]. During electrospinning, the polymer solution jet goes through the following stages: Taylor cone (appearance of the jet), straight-line stationary flow, unstable movement, and final formation of the polymer fiber with its deposition on the substrate.

Among the numerous types of degradable polymers, polylactide is currently the most promising. Polylactide (PLA) is a biocompatible, thermoplastic, biodegradable aliphatic polyester whose monomer is lactic acid [3, 4]. In recent years, the production of such polymers has been growing continuously and seeks to replace polymer materials that are resistant to the environment as much as possible. Another advantage of PLA is that it can be obtained from completely renewable natural materials [5, 6]. Since polylactide has a complex ester group, it can gradually hydrolyze under relatively mild conditions. During the hydrolysis of polylactide, lactic acid is formed, so it is believed that the use of materials based on this polymer does not cause damage to the biosphere.

Another promising, biodegradable polymer, which will be the subject of this work, is poly-3-hydroxybutyrate [7]. Poly-3-hydroxybutyrate (PHB) of various molecular weights is prepared microbiologically using different bacterial strains, for example, the PHB-producing strain Azotobacter chroococcum 7B. 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 [8].

In this study the fibrous materials of PLA and PLA-PHB were obtained by electrospinning and their thermal properties and application as agrofiber materials were investigated.

2. 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 2.5×10^5 g/mol, a melting point (T_m) of 175–180°C, and a density of 1.25 g/cm³. To prepare the spinning solutions (7 % polymer content), chloroform of reagent grade was used. The content of PHB in the composition was 10 wt. %. Polylactide (Nature works 4032D, USA) with a molecular mass of 1.7×10^5 g/mol and a melting point (T_m) of 163–165°C, and a density of 1.24 g/cm³ was used. The fibers were obtained by electrospinning.

Germination of seeds Seed quality was determined in accordance with GOST 12038-84 (Agricultural seeds. Methods for determination of germination). Seeds were placed in Petri dishes on filter paper without touching each other. For each variant of the experiment, 100 seeds were used in each Petri dish in 4-fold repetition. After three days, the seed germination energy was determined, and after 7 days, the germination rate was determined. Seeds of winter wheat (Triticum aestivum L.) of the "Athena" variety were sown on the polymer substrates and were sprouted according to GOST12038-84. Sampling took place on the same day, the number of plants taken for measurements was 20 for each sample.

Differential Scanning Calorimetry 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±0.3 mg. The temperature scale was calibrated against an indium standard (T_m = 156.6°C, ΔH = 28.44 J/g). For PLA ΔH^* = 93.1 J/g and for PHB ΔH^* = 146 J/g were used.

Photographs To obtain the photographs the Canon camera DS 126181 (Japan) was used. Then the photos are processed in Microsoft Word program.

Degradation in soil Biodegradation test in soil was carried out at T= 20±2 °C in a laboratory. 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.

3. Results and discussion

Special requirements are imposed on the seed carrier material or seed Mat [9]. The fibrous material must be non-toxic, since it is in direct interaction with biological objects – plants. It must have the ability to degrade under the influence of various environmental factors. To ensure germination, growth and development of plants, it is necessary to model the structure of the material in such a way that it supports the diffusion of water and minerals. To achieve the above requirements, non-woven fiber samples of PLA and PLA-PHB were obtained. The purpose of the work is to study the effect of non-woven fiber made of polylactide and poly-3-hydroxybutyrate on the sowing properties of grain seeds. Thus, the seeding qualities of wheat seeds were determined in laboratory conditions. The seed quality obtained in this experiment was high for all samples. Germination rate was 98% in the control sample and 99 % when germinating seeds on non-woven material (figure 1). But it is not only the seed quality that is important, but also the growth and development indicators of wheat.
Figure 1. Energy of germination and germination of winter wheat (Triticum aestivum L.) of the "Athena" variety, obtained according to GOST (control) and on polymer non-woven fiber PLA and PLA-PHB.

Then, after 12 days, biometric indicators of wheat plants were determined. The numerical data is presented in table 1. To calculate the average parameters, plants were taken in the amount of 20 pieces for each sample.

Table 1. Biometric indicators of 12-day wheat plants sprouted using GOST (control) and polymer non-woven materials.

| Sample      | Plant weight, g | Root weight, g | Root length, sm | Sprout height, sm |
|-------------|-----------------|----------------|-----------------|-------------------|
| Control     | 0.176           | 0.054          | 9.8             | 11.9              |
| PLA         | 0.198           | 0.060          | 13.1            | 12.7              |
| PLA-PHB     | 0.195           | 0.058          | 12.5            | 12.4              |

Note: the standard error of the average did not exceed 7%.

It is noticeable that all the indicators of the control sample shown in table 1 are lower than in the case of non-woven materials. The observed effect is most likely related to the hydrolytic degradation of non-woven fibers.

Table 1 shows that the mass of plants sprouted on polymer carriers made of biodegradable polyesters is higher by 0.022 and 0.019 grams for PLA and PLA-PHB samples, respectively. The height of plants grown on fibrous materials is also higher than in the control sample. The root system of plants also reacts to the presence of non-woven fiber. The length of wheat roots in the control sample is less than 0.5-0.8 cm of the length of the roots of plants sprouted on non-woven fibers.

Why can this effect be observed? It is known that natural polyesters undergo a hydrolysis process. In this experiment, during hydrolysis of PLA, lactic acid is formed, which is a nutrient for wheat plants. In addition, the root system of wheat during growth secretes enzymes that interact with the polymer matrix. Due to the processes described above, non-woven fiber materials are destroyed.

Then a soil test was performed. 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_w 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 hydrolytic degradation
and biodegradation by microorganisms. Active biodestructors are mold (*Aspergillus Niger, Penicillium Chrysogenum* and *Trichoderma Viride*), which quickly damage polymeric materials based on natural polyesters [10].

**Figure 2.** Photographs of PLA-PHB non-woven fiber after degradation in soil for 60 days. Size of the pieces is about 1×1.5 sm.

In our experiment, after 60 days of soil exposure (T= 20±2 °C), the samples of nonwoven fibers PLA and PLA-PHB lost about 10 and 21 wt.% and collapsed into fragments (figure 2). In figure 2 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.

| Table 2. Thermophysical characteristics of the initial samples of non-woven fibers PLA and PLA-PHB before and after degradation. |
|---|---|---|---|
| Sample | $T_m$, °C | $\chi_c$, % | |
| | initial | after degradation | initial | after degradation |
| PLA | 164 | 158 | 40 | 35 |
| PLA-PHB | 163/171 | 156/- | 39/56 | 30/- |

One can see that during the experiment the thermophysical characteristics of non-woven fibers undergo changes. The melting temperature ($T_m$) of both samples is reduced by 7-8 °C, there is a significant decrease in the value of degree of crystallinity. Moreover, for the PLA-PHB sample, the change in the PLA $\chi_c$, value is 9 %, and the melting peak of PHB is generally absent, which indicates the fracture of the crystal structure and the processes of degradation.

4. Conclusion

Non-woven fiber materials PLA and PLA-PHB were obtained by electrospinning. An experiment was conducted on germination of grain crops – winter wheat (*Triticum aestivum* L.) of the “Athena” variety on substrates made of non-woven agrofibres. High values of sowing qualities of wheat seeds – 98-99% were found. It was determined that the biometric indicators of wheat plants grown on polymer fibrous materials were higher than the control values, and the root system of plants was better developed. Root weight and root height of wheat grown on polymer samples were elevated.

Under the influence of the aqua medium and enzymes secreted by the root system, non-woven agrofibres undergo a process of degradation, what is a positive effect.
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