

Effect of water and soil microbiota on structure and properties of PLA fiber composites

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Abstract. Nonwoven fibers from biodegradable polymers such as polylactide and natural rubber were obtained by electrospinning. The fiber morphology was studied by optical microscopy. Thermal properties were studied by differential scanning calorimetry. It is shown that after the action of water for 180 days, the glass transition temperature is not observed on DSC thermograms. The degree of crystallinity of all samples increases by 9-12% depending on the composition. After exposure to soil, the glass transition temperature changes little for pure PLA and a sample containing 5 wt.% of natural rubber and decreases by 2-3 oC in samples with a rubber content of 10 and 15 wt.%. The melting point of PLA fiber increases by 2 oC during degradation in the soil, and in fibrous composites it decreases by 1.5 oC. Changes in the values of the degree of crystallinity have a similar tendency. Thus, under the same temperature and time conditions, water has a stronger effect compared to soil on the structure of nonwoven fibrous materials PLA/NR. **Key words:** biodegradable polymers, nonwoven fibers, polylactide, natural rubber, soil microbiota.

1 Introduction

Advanced composite materials have been increasingly used in aviation, aerospace, automobile. Over time, the performance properties of all polymer materials change. Under the influence of temperature, air oxygen, mechanical stresses, ionizing radiation and other factors, polymers undergo aging. Processes occurring in polymer materials, accompanied by changes in their chemical and physical structures. Previously, the issue of polymer stabilization was acute, nowadays the environmental aspect has become very important. Now the focus is on biodegradable and eco-friendly polymers and polymer composites [1, 2]. Such materials are destroyed in the environment without the formation of toxic products. One of these polymers is polylactide (PLA).

Poly lactide is one of the most promising biobased and biodegradable polymers for food packaging, an application which requires good mechanical and barrier properties. It can be used as good alternative to the petroleum-based commodity materials, because it can be

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derived from renewable resources, such as corn, potato, and other agricultural products [3-7]. Moreover, PLA has good thermoplasticity, high degree of transparency and biocompatibility. However, some of its properties, like flexural properties, gas permeability and heat distortion temperature, are too poor for widespread applications. In order to improve the mechanical properties, in particular the flexibility, another component is required [8, 9].

Natural rubber has been used for the PLA modification [10-14]. Natural rubber (NR) is an elastomer derived from latex, which is obtained from the rubber tree juice. Natural rubber, deemed to be a strategically significant material, has received great attention in the industrial, medical, and agricultural fields for a long time owing to its unique physical and chemical properties. Polymer nonwoven fibers based on polylactide and natural rubber (PLA/NR) were obtained by electrospinning from a solution. Electrospinning is a complex process involving the hydrodynamics of low conducting Newtonian fluids and phase transformations of polymers [15]. Optimization of the electrospinning process makes it possible to obtain ultrathin non-woven fiber of high quality.

In this work, the hydrolytic degradation and damage of PLA/NR fibrous materials under the action of soil microorganisms were studied. The study of these processes in relation to biodegradable polymers is always relevant. All polymer composites are somehow exposed to humidity or directly to water. Hydrolysis is the nonbiological degradation. It occurs at a slow rate but is enhanced by acidic and alkaline conditions. There is an apparent initial increase in crystallinity, when the extent of hydrolysis increases, which is followed by a decrease in crystallinity and an elevated rate of hydrolysis.

The authors [16] studied the hydrolytic degradation of PLA and its composites in deionized water at $T = 37$ °C and found that the hydrolysis process is most active after 3 months of exposure to deionized water. Researchers [17] considered the effect of crystallinity and micro- and nanoscale clay on the degradation of PLA at a temperature of 50-70 °C. The paper shows that the degradation rate constants were higher for amorphous PLA compared to semi-crystalline, and also that micro-sized clay slows down the process of hydrolysis of PLA, and clay nanoparticles accelerate it. In [18], phosphate buffer solutions were used to study the process of hydrolytic decomposition. Hydrolysis was carried out for a period of 7 to 30 days at a temperature of 60 °C in two buffers: phosphate–buffer solution (pH 7.40) and phosphate-lemon buffer solution (pH 7.40). The results obtained showed that the type of buffer solution significantly affects the hydrolytic degradation of the PLA and its composites.

Biodegradation in soil normally proceeds surface attack by molds and bacteria. But water is part of the biodegradation process in the soil since well-watered soil is used in the experiment.

2 Materials and methods

For producing of fibrous material 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. Natural rubber (NR), SVR-3L with Mooney viscosity 50 ± 5 (100 °C), poly(cis-1,4-isoprene) content: 91-96, wt.% and volatiles – 0.8 wt.% was kindly supplied by Vietnam Rubber Group (Vietnam). The polymer solutions for electrospinning were prepared by dissolving PLA and PLA/NR in the right ratio in chloroform. The mixtures were heated at 60 °C for about 4-5 min. The polymer solution was placed in a syringe with a needle inner diameter 0.7 mm, set up vertically. The electrospinning experiments were performed at room temperature (20 ± 2 °C).

Square film samples with a side of 30 mm were used for hydrolytic test during 180 days. The test was carried out on at least 3 samples of each composition. Before the test, the samples were dried at (40 ± 2) °C for 24 hours, and then cooled in a desiccator over a desiccant - calcium chloride at (22 ± 2) °C.

In the same containers with 200 ± 20 g of soil of the brand "Soil Keva for Vegetables" (Gera, Russia), pH 5.5 – 7.0 samples of nonwoven materials were placed. The containers were kept at a temperature of $22 \pm 2^\circ\text{C}$ with well-watered soil. The soil was moistened as needed. The duration of the test was 180 days.

Thermal analysis was performed by differential scanning calorimeter (DSC) using a DSC 204 F1 device (Netzsch, Germany) under a nitrogen atmosphere. Samples of about 5.0-5.4 mg sealed in aluminum pans were heated from room temperature to 200°C at rate of $10^\circ\text{C}/\text{min}$. Indium with $T_m = 156.6^\circ\text{C}$ was used as a calibrant. The crystallinity of PLA (χ_c) was estimated from the first heating cycle using the following equation:

$$\chi_c = \left(\frac{\Delta H_m}{\Delta H_m^*} \right) \times 100 \quad (1)$$

Where ΔH_m is the enthalpy of melting during heating, ΔH_m^* is the enthalpy assuming 100% crystalline PLA homopolymer 93.1 J/g [19].

The morphology of the fiber materials was studied by optical microscopy. The micrographs of the specimens were taken with an Axio Imager Z2m optical microscope (Carl Zeiss, Germany) using Axio Vision software at magnifications 100.

3 Results and discussion

The thermophysical characteristics of nonwoven PLA and PLA/NR fibers with different NR content were determined by the DSC method before and after degradation in the soil and water for 180 days (Fig. 1).

In the initial composites, the glass transition, cold crystallization and melting temperatures increase with an increase in the NR content in the polylactide matrix. The degree of crystallinity also increases. Apparently, natural rubber increases segmental mobility and facilitates the process of crystallization of polylactide.

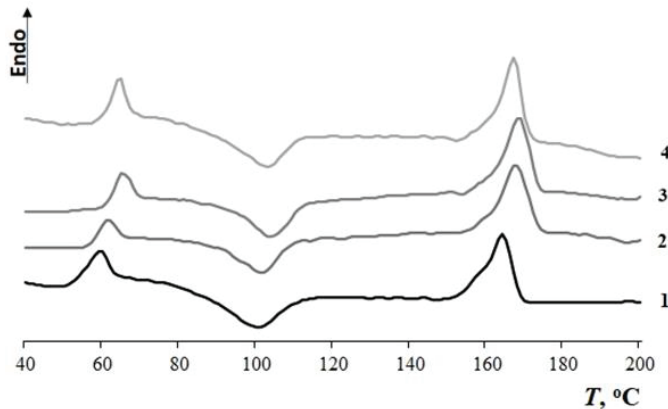


Fig. 1. DSC thermograms of initial PLA/NR samples with different NR content, wt.%: (1) – 0; (2) – 5; (3) – 10; (4) – 15.

When studying the effect of water on non-woven fiber PLA/NR for 180 days, it was determined that after hydrolytic degradation on the melting thermograms, the melting temperature (T_m) of PLA/NR samples changes insignificantly and the glass transition peak of PLA almost disappears (Fig. 2).

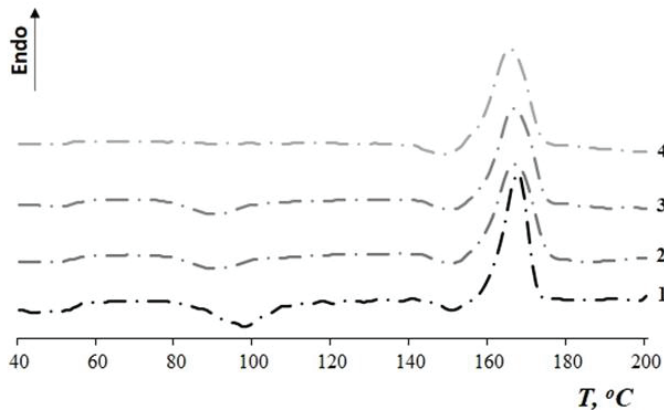


Fig. 2. DSC thermograms after hydrolytic degradation for 180 days of non-woven PLA/NR fibers with different NR content, wt.%: (1) – 0; (2) – 5; (3) – 10; (4) – 15.

The degree of crystallinity of all samples increases by 9-13 % depending on the composition. An increase of the PLA degree of crystallinity is a consequence of the disintegration of the amorphous phase and such behavior of T_g is attributable to a decrease in molecular weight. After soil exposure for 180 days the DSC thermograms view is different from those after water influence. The thermograms show clear peaks in the temperatures of glass transition, cold crystallization and melting (Fig. 3).

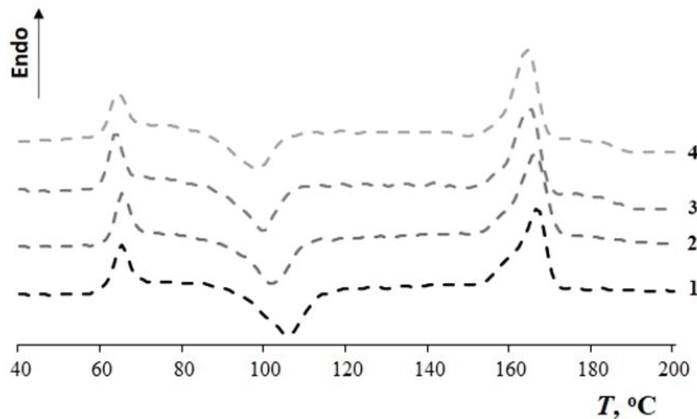


Fig. 3. DSC thermograms after degradation in soil for 180 days of PLA/NR samples with different NR content, wt.%: (1) – 0; (2) – 5; (3) – 10; (4) – 15.

The values of T_m and T_g in samples of fibrous PLA/NR of all compositions tends to decrease, and in 100% of PLA to increase. Usually, during the disintegration of the polymer, the value of the glass transition decreases. Probably, in this experiment for 180 days, the degree of degradation of PLA is not deep enough and a process similar to polymer annealing is observed. Although water is present in the soil and significant changes in thermal characteristics could be expected, the results obtained are somewhat different. The change in the degree of crystallinity after degradation in the soil is lower than in the process of hydrolytic action. For clarity, all numerical data are summarized in Table 1.

Table 1. DSC results of initial samples and after degradation in water and soil.

NR content, %	$T_g, ^\circ\text{C}$			$T_{cc}, ^\circ\text{C}$			$T_m, ^\circ\text{C}$			$\chi_c, \%$		
	initial	water	soil	initial	water	soil	initial	water	soil	initial	water	soil
0	61	-	62	101	98	105	164	168	166	33	46	36
5	63	-	64	102	93	103	168	167	166,5	36	46	35
10	66	-	63	105	93	101	167	167	165,5	37	47	35
15	65	-	63	104	-	100	166	166	164,5	36	47	34

Cold crystallization temperatures have a different tendency after the action of water and soil microbiota. The peak of crystallization practically disappears after hydrolytic degradation (Fig. 2) and in the sample of composition 85/15, the T_{cc} value is not fixed, which is most likely due to the disintegration of the amorphous phase and the defect of the crystal structure. After biodegradation the T_{cc} of samples containing 10 and 15 wt.% NR also decreases, but not as significantly as in the process of hydrolytic exposure.

Micrographs after 180 days of biodegradation in the soil were obtained by optical microscopy and are shown in figure 4.

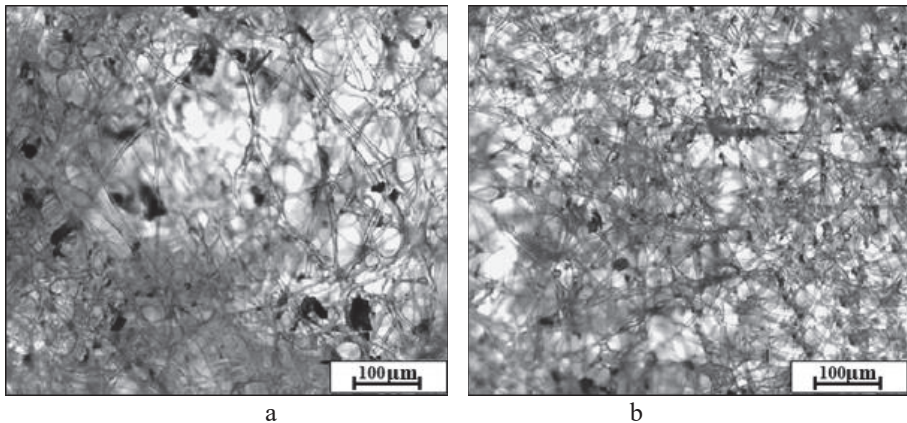


Fig. 4. Micrographs after 180 days of biodegradation: (a) – pure PLA fiber, (b) – the sample with 5 wt.% of NR content.

After the experiment in the soil, the fibrous samples were thoroughly washed. According to Fig. 4, the dark spots that are visible on microphotographs are a consequence of the action of the soil microbiota: bacteria and mold fungi. It is known that such kinds of micromycetes as *Aspergillus*, *Trichoderma*, *Penicillium* are present in the soil. It should be noted that both polymers, both PLA and natural rubber, are broken down by microbiota. There are works in which the ability of natural rubber to biological degradation has been studied [20].

4 Conclusions

Poly lactide is polymer obtained from renewable raw materials as well as natural rubber. Eco-friendly and promising biodegradable PLA/NR fibers are obtained and studied. The thermophysical characteristics of the initial fibrous materials and after degradation in water and soil were determined by the DSC method.

Water plays a crucial role in biological processes but can adversely affect the performance of polymers. Differences in the thermograms of the samples are shown. The glass transition temperature is not fixed after the action of water and the degree of crystallinity of nonwoven fibers increases significantly. It is established that the hydrolysis of PLA begins with the diffusion of water molecules into amorphous regions. It is possible that the disintegration of the amorphous phase during hydrolytic degradation occurs more actively than in the case of degradation in the soil. At the same temperature all thermophysical characteristics change much less after biodegradation in the soil than when exposed to water for 180 days. Perhaps because the activity of the microbiota increases with an increase in temperature to 28-35 °C.

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