Aging of PLA/NR electrospun fibers under the influence of UV- irradiation, water and soil environment

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Abstract. Research in the field of the influence of environmental factors on composite materials based on polyesters is very relevant, as such materials are gaining more and more use in various industries and agriculture. This paper presents the results of the influence of UV-irradiation, water and soil on PLA/NR nonwoven fibers. The content of NR was 5-15 wt.%. It was found that the presence of NR over 10 wt. % inhibits photolysis. After 300 hours of irradiation, the melting point of 100% PLA decreases more significantly than in composites with NR. The IR-spectroscopy method confirmed the occurrence of the process of photooxidative degradation in fibrous samples. Biodegradation in soil proceeds more actively in PLA/NR fibrous composites than in pure PLA. Apparently, an increase in the proportion of the amorphous phase in the composites and the bioavailability of rubber contribute to this process.

1 Introduction

With the development of global plastics technology, the annual production of plastics has reached approximately 450 million metric tons in recent years, resulting in more than 340 million tons of plastic waste, which puts enormous pressure on the environment [1]. By 2050, it is estimated that 26 billion metric tons of post-consumer plastic waste will be generated, half of which will be released into the environment, creating an ongoing waste management problem [2].

A large amount of plastic waste from mulching films has accumulated in the topsoil of agricultural fields around the world. The costly, time-consuming and laborious task of removing these films, combined with the slow mineralization of traditional plastics used for mulch film, has resulted in an increase in waste over the past few years. Thus, post-harvest mulching film can have an adverse effect on the soil, for example, affect crop yields in subsequent years [3-5].

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In response to this problem, biodegradable mulch materials are being developed, both film and non-woven, based on biodegradable polymers such as polylactide (PLA), polycaprolactone (PCL), polyhydroxyalkanoates (PHAs), polybutylene succinate (PBS) [6, 7].

PLA fibrous material can serve as covering fabrics for growing new experimental varieties in breeding and seed production or serve as substrates for growing various crops. Modern trends focused on eco-friendly technologies are leading to increasing use of biodegradable polymers in agricultura. This is especially true for crop production, which uses covering and mulching polymer materials, a significant part of which enters the soil directly during their use, bypassing the stages of collection, sorting and processing [8].

Thus, in [9, 10], the production of PLA/PP nonwoven material was discussed, but the poor compatibility of PLA and PP limits its industrial application. Blending polymers with other polymers with surfactant structure, organic or inorganic materials to obtain composite materials with good mixing effect and tensile property is one of the common methods to improve the compatibility of incompatible materials.

Among the biodegradable polymers, polylactide is actively researched and a large number of compositions are being developed on its basis. Polylactide (PLA) is a linear aliphatic polyester obtained in two stages. First, themonomer lactic acid is released during the fermentation of waste vegetable raw materials. At the next stage, polylactide is obtained from lactic acid by polymerization [11, 12]. PLA is a biodegradable and biocompatible thermoplastic; it is produced on a large scale and used for various applications in different industries, such as medicine, packaging and agriculture [13–15].

Due to the fact that materials based on polylactide can be used in agriculture, it is extremely important to study the influence of UV radiation, water and soil microorganisms. If the polymeric material enters the soil, then, along with the soil microbiota, it is affected by water [16–18].

At the same time, during the operation of biodegradable mulching materials, UV radiation has an aggressive effect, which rather actively affects mixtures based on PLA [19–23]. Therefore, some researchers are looking for additives that help curb the photolysis of polylactide, one of such additives may be natural rubber.The blending of PLA with other polymers is less expensive and more practical. Rubber has been used as a second-phase polymer to toughen brittle thermoplastics. The authors [24] reported that the ductility of PLA was significantly improved by blending it with NR. The amount of NR at 10% weight seems to give an optimum property. Nonwoven PLA/NR fiber has an increased elasticity compared to that of 100% PLA, while remaining eco-friendly and biodegradable.

The aim of this work is study of the process of disindegration of PLA/NR non-woven fiber under the action of UV-irradiation, water and soil microbiota.

2 Methodology and materials of the experiment

The object of research in this work 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 (Tm) of 163–165 °C was used. Natural rubber (NR), SVR-3L with Mooney viscosity 50±5 (100 ºC), 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 ºC 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 ºC).

Methods of structural analysis. The morphology of the initial PLA and PLA/NR fibers and after degradation was characterized by scanning electron microscopy Philips SEM-500

(Eindhoven, The Netherlands) at different magnifications. The surface and lateral sections of the samples were examined.

DSC analysis is a method DSC 214 Polyma (Netzsch, Германия) при скорости нагрева 10 град/мин и массе образца (10±0,1) мг. Melting enthalpy of 100% polylactide crystal $\Delta H_{пл}{}^{*}$= 93 Дж/г.

IR analysis. The infrared spectra of the samples were recorded on a Lumos Bruker IR-Fourier spectrometer (Germany) at T = (23 ± 2) °C in the wavenumber range 4000 ≤ ν ≤ 600 cm-1 (ATR)

UV. The resistance of samples to photodegradation was studied using a VL-6.LC ultraviolet radiation source from Viber Lourmat (France) with a wavelength of 365 nm, exposure time was 300 hours.

Hydrolysis. 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.

Biodegradation in soil. 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±2 ºC with well-watered soil. The soil was moistened as needed. The duration of the test was 180 days.

3 The results of experiments and discussion

An important place is occupied by studies of the destructive processes of polymer composites based on PLA. There are many works that study hydrolysis [12], biodegradation [16], and photodegradation upon exposure to ultraviolet radiation of various wavelengths [23].

The study of degradation of composites is important not only from the point of view of the material durability during its life, but is also of paramount importance from the point of view of the post-operational period. The degradation of PLA leads to a decrease in molecular weight, color change and loss of mechanical characteristics. The presence of additives in the polylactide matrix can either enhance the photodegradation process or block it. The photodegradation of PLA biocomposites is highly dependent on the content of fillers and their nature. Aggregation of fillers can lead to accelerated degradation due to more structural defects that facilitate the degradation process. In this part of the study, it is important to determine the effect of NR on the photodegradation of nonwoven PLA/NR fibers, and the addition of NR-content increases or decreases the resistance of nonwoven fibers to UV radiation, which is very important for covering material used in open-ground conditions.

In [24], the degradation of a nonwoven material based on PLA with the addition of natural rubber under the action of UV-irradiation with a wavelength of 365 nm, which corresponded to softer radiation, was studied. Under these conditions, the amorphous phase decomposed and the degree of PLA crystallinity increased in PLA/NR samples could be observed after 50 hours of UV exposure. It is possible that exposure to such a wavelength of UV- radiation causes an annealing effect in which the glass transition temperature, melting point, and degree of crystallinity increase. The authors suggest that with further experiment, the thermal characteristics of pure PLA will begin to decrease.

As a result of the UV influence (λ = 365 nm) for 300 hours on PLA/NR fiber composites, it was found that the beginning of the PLA/NR degradation occurs. This is noted on the change in the IR- spectra (Fig. 1).

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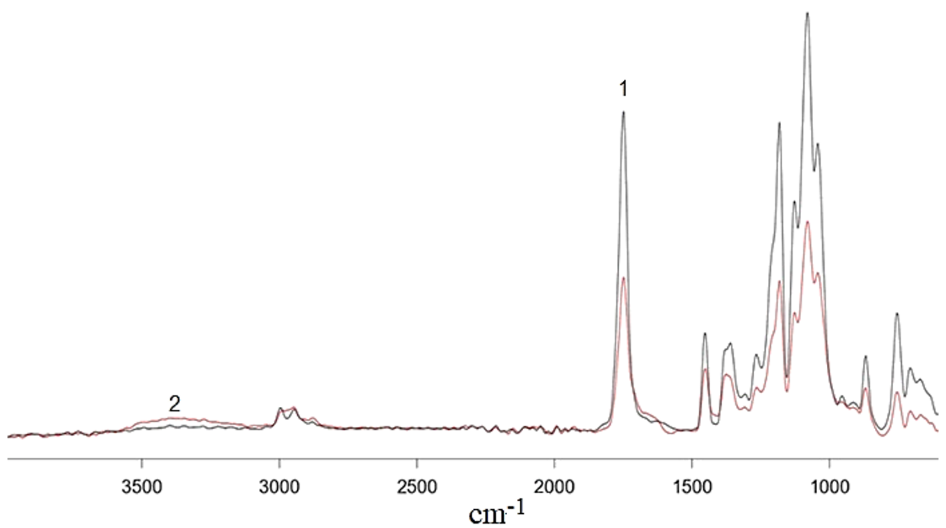


Fig. 1. FTIR spectra of PLA/NR fibers with the NR content 15 wt.%: initial (1) and after 300 h of UV-irradiation (2).

In the IR spectra in the compositions with rubber, an increase in the intensity of the bands in the region of 3600–3050 cm^{-1} is noticeable (Fig. 1), which indicates the accumulation of hydroxyl groups formed during the oxidation of polyisoprene. In all PLA/NR samples, after exposure to UV, the intensity of the remaining structurally sensitive bands decreased. The absorption bands at 1380–1000 cm^{-1} refer to spatial fluctuations of –C–O groups. In the range of 1900–1600 cm^{-1}, a peak at 1745 cm^{-1} is distinguished, which belongs to the –C=O groups. The decrease in the intensity of these bands, apparently, occurs due to the elimination of ester groups in the course of degradation. The bands at 755 and 870 cm^{-1}, corresponding to the crystalline and amorphous phases of PLA, are also less intense after photodegradation.

The DSC method confirms the change in the structure of the PLA/NR composites. The thermophysical characteristics of PLA and PLA/NR samples were determined by DSC before and after UV exposure.

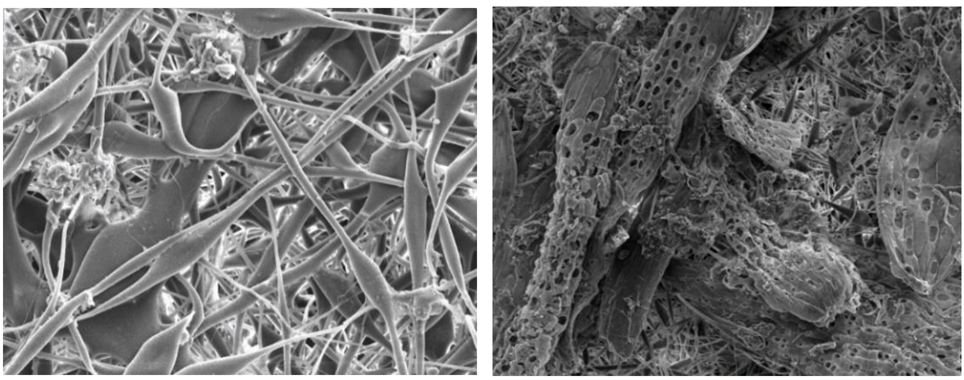
Table 1. Thermophysical characteristics of PLA/NR fiber composites before and after exposure to UV radiation (λ = 365 nm) for 300 hours.

Composition of PLA/NR, wt %	**Tm, °C ±0,1 °C**	**χ, % ±0.5%**	**Tm, °C ±0,1 °C After 300h**	**χ, % ±0.5% After 300h**
1	2	3	4	5
100/0	164	33	159	29
95/5	168	36	163	31
90/10	169	37	166	35
85/15	169	37	167	34

A decrease of T_m by 2-5 °C, and a decrease in the degree of crystallinity by 3-5% indicates the degradation of the PLA crystal structure. On the other hand, the presence of natural rubber in the composition in an amount above 10 wt.% contributes to a slight inhibition of photolytic processes, which can positively affect the property of the material during operation.

As mentioned above, when PLA/NR nonwoven fibers are used in agriculture, for example, as substrates for growing crops, there is a direct interaction not only with the soil, but also with the aquatic environment. Samples of PLA/NR fibers were kept in soil for 180 days and then also examined.The microphotographs (Fig. 2) show a surface of the investigated fibers.

In the process of degradation in the soil, a certain pattern of changes in the thermophysical values of pure PLA and samples of PLA/NR non-woven fiber was noticeable.



a *b*

Fig. 2. Scanning electron micrographs after 180 days of soil exposure of PLA/NR samples with NR content, wt.%: 5 (a) and 15 (b).

The degradation of PLA/NR composites in the soil proceeds quite actively. Due to the bioavailability of NR and the increase in the total amount of the amorphous phase in the presence of rubber, the 85/15 sample is most susceptible to biodegradation in soil. After degradation in the soil, microcracks, holes and roughness are noticeable.

Table 2. Thermophysical characteristics of PLA/NR fibers before and after soil exposure for 180 days.

Composition of PLA/NR, wt %	**Tm, °C ±0,1 °C**	**χ, % ±0.5%**	**Tm, °C ±0,1 °C After 180 days**	**χ, % ±0.5% After 180 days**
1	2	3	4	5
100/0	164	33	166	37
95/5	168	36	166	35
90/10	169	37	165	35
85/15	169	37	164	33

Water is one of the aggressive agents of damage to polymeric materials. It is able to penetrate the surface layers of the material and diffuse deeper. The study of water absorption and the kinetics of this process makes it possible to analyze structural features and predict changes in the process of biodegradation of composites. The water absorption by polymers depends on many components. For example, the degree of crystallinity and the temperature play an important role. The degree of water absorption is very dependent on the type of material. It is obvious that due to the porous structure, the fiber absorbs more water than the film. In this case, it is the type of material that plays the main role, and not the hydrophilicity or hydrophobicity of the polymers in the composite. The addition on NR reduces the degree of water absorption of PLA/NR samples compared to 100% PLA by several percent. Apparently, the beaded morphology formed in the PLA/NR fibers somewhat hinders the absorption of water (Fig. 3). Hydrolysis of PLA occurs by the addition–elimination of a complex carbonyl induced by water, and then water-soluble oligomers and monomers are produced. In the process of hydrolytic degradation, the samples turn white. Such an effect was also observed for PLA/NR fibers.

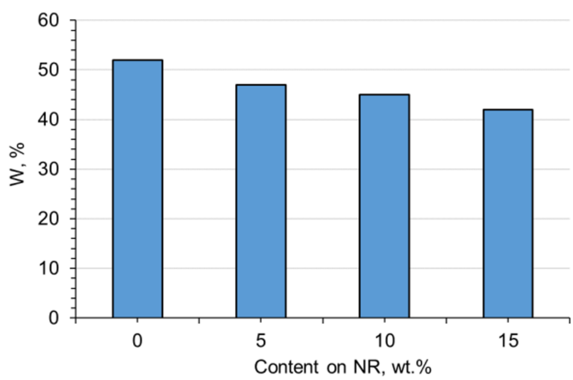


Fig. 3. Degree of water absorption (W, %) of PLA/NR fibers with 0, 5, 10, and 15 wt.% of NR content.

It is obvious that NR influences the process of PLA degradation. Melting and glass transition temperatures in samples of fibrous PLA/NR of all compositions tend to decrease, and in 100% of PLA, increase. Usually, during the disintegration of the polymer, the value of the glass transition decreases. Degradation in the soil is the action of water, temperature, bacteria and molds at the same time. It should also be noted that the rapid acceleration of the degradation of such materials in the soil can be achieved by increasing the possibility of surface penetration of enzymes, i.e., by increasing the specific surface area, and especially wettability [25, 26] NR is unlikely to increase wettability, but it does increase the proportion of the amorphous phase in the PLA/NR fiber composites, increasing the vulnerability of the polymer matrix to the effects of aggressive environments.

4 Conclusions

In this work, the influence of UV radiation, water, and soil microbiota on PLA/NR nonwoven fibers was studied. The structure was controlled by DSC and IR-spectroscopy. The highest degree of water absorption is observed for pure PLA which can be explained by the peculiarities of the morphology of PLA/NR composites. It has been determined that the addition of NR to the PLA matrix accelerates the degradation process in the soil by increasing the content of the amorphous phase in the composites and the bioavailability of natural rubber.

The effect of photooxidation on pure polylactide and the properties of composites with the addition of natural rubber in an amount of 5-15 wt.% were studied at a wavelength close to natural conditions. It has been established that pure PLA undergoes photodegradation more actively than in composites. It has been determined that the presence of NR in a mixture of more than 10 wt.% can help slow down the photodegradation of compositions.

Thus, depending on the application and the required performance, less or more resistant PLA/NR fiber composites to UV- aging can be used.

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