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COMPOSITION MATERIALS BASED ON POLYLACTIDE WITH LIGNIN FOR PRODUCTION OF BIODEGRADABLE PACKAGING

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Abstract. Polymer composite materials based on polylactide, have been developed for the production of biodegradable packaging films and plastic sheets. To regulate their properties and resistance to natural factors, soil lignin filler is introduced into the composition. The results of the investigation are presented on the structure, physical and mechanical properties and resistance to UV-radiation and hydrolytic degradation.

1.   Introduction

A special class of modern packaging materials that can compete with cardboard products in the future is made up of cheap, eco-friendly plastics – biodegradable polymers that are being introduced into production and are gradually beginning to replace traditional plastics. Biodegradable polymers are obtained from renewable plant materials – corn, potatoes, wheat, beets, hardwoods, which can be used almost continuously (Banerjee & Sinha, 2021) (Balart *et al*., 2021). For example, a packaging made of polylactide (PLA) can completely decompose within 45 days, subject to the creation of an appropriate composting structure (Badia & Gil-castell, 2019) (Kale *et al*., 2006a).

In the production of packaging and disposable products in contact with food, polylactide is used without any additives in order to maintain its transparency. On its basis it is also possible to create composite polymer composition materials (CM), primarily with polyolefins and polystyrene, which are most often used for the production of packaging and are characterized by extremely high chemical resistance (Aworinde *et al.*, 2021) (Norazlina *et al*., 2021) (Kale *et al.*, 2006a). The creation of biodegradable composites with the required properties will significantly solve the problem of recycling the growing of household waste (Kale *et al*., 2006b) (Avinc & Khoddami, 2009). To reduce the cost of the final material, increase the competitiveness of products, it is necessary to optimize and (or) change existing production technologies (Auras *et al*., 2004) (Gumienna & Górna, 2021). A control the physical and mechanical properties, chemical resistance and resistance to natural factors, for example, to UV radiation and changes in pH, is possible by adding organic or inorganic fillers (Tertyshnaya *et al*., 2021) (Dreier *et al*., 2021).

In the general, photodegradation of polymers is a complex multistage process. The introduction into the polymer matrix of light stabilizers, which absorb part of the reactive light and convert it into heat, prevents photodegradation.

Derivatives of o-hydroxybenzophenone, benztriazole, triacetonamine are used as light stabilizers. In some cases, photostabilization can be carried out by a photochemical reaction in a polymer matrix. Phenols, which are part of lignin (Vanholme *et al*., 2010), convert the energy of radiation into a substitution reaction, leading to the formation of hydroperoxide, a potential source of radicals (Ralph, 2010). Under the conditions of photooxidation, nitroxyl radicals also terminate the chain by reaction with alkyl radicals. At the same time, electronically excited nitroxyl radicals are capable of initiating the oxidation of polymers. During the photooxidation of polymers, nitroxyl radicals can extinguish excited shapes and absorb the energy of light radiation (Olewnik-Kruszkowska *et al.*, 2015).

The work investigated extrusion methods for producing CM in the form of films and sheets. The main task was the manufacture of various materials suitable for production, as well as the study of their structure, physical and mechanical properties, resistance to water and UV radiation.

2.   Materials and methods

Commercially available PLA *INGEO 4043D* (USA) was chosen as the basis for the composite materials. To create composites, lignin was used as a filler. The production of film and sheets was carried out by the method of flat-slit extrusion. The extruder consists of 5 sections of the material cylinder with independent heating and cooling and precise temperature control in each of them. The mixing of the components of the mixture was carried out mechanically, and the final homogenization took place in the material cylinder of the extruder. Table 1 shows the temperature distribution by zones of the material cylinder and the temperature of the mold.

Table 1. Processing temperatures of compositions based on polylactide

Mold temperature	Nozzle	4	3	2	1	In the loading zone
50	185	185	185	185	150	150

Lignin (Bobruisk Biotechnology Plant, Belarus) was used with a particle size of 0.06 and 0.16 mm and a density of 1.25-1.45 g/cm^3. During the film production, lignin was mechanically mixed with PLA in the presence of PMS 100 silicone oil, which was added to improve the adsorption of lignin on the surface of the granules.

Before preparing the mixtures, the required amount of PLA was placed in a drying hopper and dried for 2 hours at a temperature of 50 °C. Table 2 shows the compositions of PLA-based CMs for the preparation of film samples.

Table 2. Compositions of CM based on PLA

Name	Characteristics of filler	Binding agent
PLA		
PLA/L 5-0,06	Lignin, particles 0,06 mm, 5,0%	PMS 100
PLA/L 10-0,06	Lignin, particles 0,06 mm, 10,0%	PMS 100
PLA/L 5-0,16	Lignin, particles 0,16 mm, 5,0%	PMS 100
PLA/L 10-0,16	Lignin, particles 0,16 mm, 10,0%	PMS 100

Characterization of CM samples. Tensile tests were carried out in accordance with GOST 14236. For testing, samples were used in the form of a rectangle with a width of 10 to 25 mm, a length of at least 150 mm on an *Instron* series 2020 tensometer at a temperature of $23.0 \pm 2.0 \,°C$ and a relative humidity $50.0 \pm 5.0\%$ at a clamping speed of 5 mm / min. Calculations of strength characteristics were performed automatically using the built-in software package *Blue Hill*. The arithmetic mean of at least five determinations was taken as the test result. The determination of the density of the compositions was carried out by the method of hydrostatic weighing in accordance with GOST 15139. (Banerjee & Sinha, 2021) on a *Mettler Toledo XS105* density meter. The melt flow rate (MFR) was measured in accordance with GOST 11645 using an *XNR-400* capillary flow index meter. The test was carried out at 190 °C and a weight of 1.25 kg, a capillary with a length of 8.0 mm, with an inner diameter of 2.095 mm. Samples for testing were selected taking into account the requirements of GOST 12423. The melt flow rate of thermoplastics MFR in 0,1g / min was calculated by the formula:

$$MFR = (600 * m)/t, \tag{1}$$

where m – the average mass of extruded segments, g;
t – time interval between two consecutive cutoffs of segments, s.

The UV-irradiation was carried out with ultraviolet lamp for 160 hours at the room temperature. At the end of the irradiation, the physicomechanical properties of the samples that had not lost their integrity were investigated.

To identify the PLA degradation products, 5 samples of PLA films with a size of 2 cm × 2 cm were examined. The material was placed in a 100 ml round-bottom flask; 25 ml of methanol was added, and stirred on a magnetic stirrer for 30 minutes. Then the solution was decanted from the residue and evaporated to dryness on a rotary evaporator. Chromatographic analysis and recording of mass spectra of the degradation products were performed by a Thermo Scientific Trace GC Ultra / DSQ II quadrupole chromatomass spectrometer with a direct injection function. Degradation products were identified using the *NIST Mass Spectral Library* 2014.

Hydrolytic degradation. To study the hydrolytic degradation of the films, polylactide films without and with lignin additives were selected. Distilled and tap water (with an initial pH value of ~ 7) was used as a hydrolysis medium.

Initial samples of 20x15 mm in size were carefully weighed before hydrolytic degradation. After that, the samples were placed in 50 ml plastic vials with screw caps filled with water. The vials were immersed in distilled water at a temperature of $60 \pm 2°C$ in an IKA HB 10 digital heating bath.

Samples were periodically removed and dried at 50ºC to constant weight. After that, the weighed portions of the samples were weighed again.

Appearance assessment and hydrolytic degradation measurements were carried out at ambient temperature. Degradation of the films was investigated by measuring the weight at regular intervals. The relative mass change in was determined:

$$W_s = (W_1 - W_2)/W_1 \times 100\%, \qquad (2)$$

where W_1 − is the initial mass of the sample, and W_2 − is the mass of the dried samples after the degradation process.

3. Results and discussion

Films were produced in a wide range of thicknesses from 0.02 mm to 0.7 mm. In thin films (less than 0.05 mm), good compatibility of the matrix (polylactide) and filler was not observed. They had low physical and mechanical properties, and a large number of pores were in their structure. Samples with a thickness of more than 0.4 mm showed a good distribution of additives throughout the sheet, however, it was not possible to maintain a uniform sheet thickness. For further testing films with a thickness of 0.08−0.2 mm were chosen. PLA film without fillers is transparent, homogeneous, with high strength properties (Figure 1).
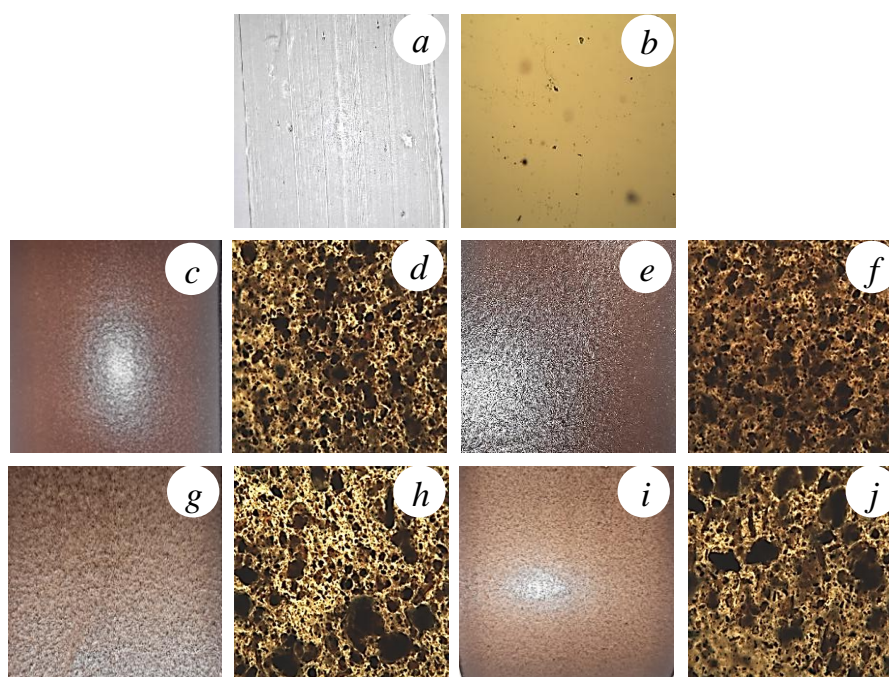

Fig. 1. Film of pure polylactide: *a* - sample; *b* - micrograph with × 20 magnification, a film of polylactide with the addition of 5.0% lignin (0.06 mm): *c* - sample; *d* - micrograph with a magnification of × 20, with the addition of 10.0% lignin (0.06 mm): *e* - sample; *f* - macro photography, with the addition of 5.0% lignin (0.16 mm): *g* - sample; *h* - micrograph with a magnification of × 20, with the addition of 10.0% lignin (0.16 mm): *i* - sample; *j* - micrograph with × 20 magnification

Films with the addition of low dispersion lignin (PLA / L 5-0.06, PLA / L 10-0.06) are smooth, brown in color, with a uniform distribution of lignin along the entire length of the film. In turn, films with high dispersion lignin (PLA / L 5-0.16, PLA / L 10-0.16) have roughness, individual particles and their conglomerates are visible on them. Films

have higher strength characteristics, which is due to the absence of pronounced structuring of the film along the direction of stretching (Table 3).

Table 3. Physical and mechanical characteristics of the samples

Sample	Without irradiation				After irradiation		
	Yield strength at break (MPa)	Elongation at break (%)	Density, g/cm^3	Melt flow rate, g/10min	Yield strength at break (MPa)	Elongation at break (%)	Density, g/cm^3
PLA	40,84	2,0	1,2218	2,30	-	-	1,1846
PLA/L 5-0,06	26,67	4,7	1,2123	2,24	3,24	0,45	1,2037
PLA/L 10-0,06	29,62	6,1	1,2160	1,78	3,97	0,48	1,2124
PLA/L 5-0,16	25,17	2,7	1,2090	2,03	5,25	0,54	1,1987
PLA/L 10-0,16	31,52	3,8	1,2098	1,86	5,12	0,43	1,1934

The presence of the additive reduces the strength characteristics of films based on polylactide. In the considered composite materials, the filler used, as a rule, increases the defectiveness and disturbs the uniformity of the film structure. All additives in the studied concentrations insignificantly affect the density of polylactide films. The values remain in the range of values suitable for the selected processing method – extrusion.

The test samples were exposed to UV-radiation, the total irradiation time of the samples was 160 hours. The samples containing lignin in their composition became brittle, covered with a sticky layer, but no visible cracks were observed, and the films of pure polylactide began to crack. Further irradiation led to significant damage. The strongest cracking and increased brittleness was observed for films of pure polylactide (Figure 2).

Results of visual analysis of destruction of samples of pure PLA in percentage terms 40 hours – 5%, 80 hours – 30%, 120 hours – 60%, 160 hours – 90%, the sample with lignin is not destroyed. Samples with lignin retained their integrity, which made it possible for them to carry out physical and mechanical tests. Table 2 shows the results of strength tests of samples of films made from CM with the addition of lignin, exposed to ultraviolet radiation (160 hours).

The strength of films based on polylactide with the addition of lignin decreased by about 10 times (Table 3), which indicates significant changes in the structure of the original film, its degradation. Determination of the density of compositions based on polylactide exposed to ultraviolet radiation was carried out in accordance with GOST 15139. A decrease in the density of the samples indicates the degradation of the films.

Thus, being a mixture of aromatic polymers, including phenylpropane elements capable of absorbing ultraviolet radiation, additives of lignin and dyes based on it are capable of inhibiting photooxidative degradation.

For a sample made of pure PLA, subjected to 160 hours of ultraviolet irradiation, a mass spectrometric analysis of the destruction products was carried out (Figure 2).
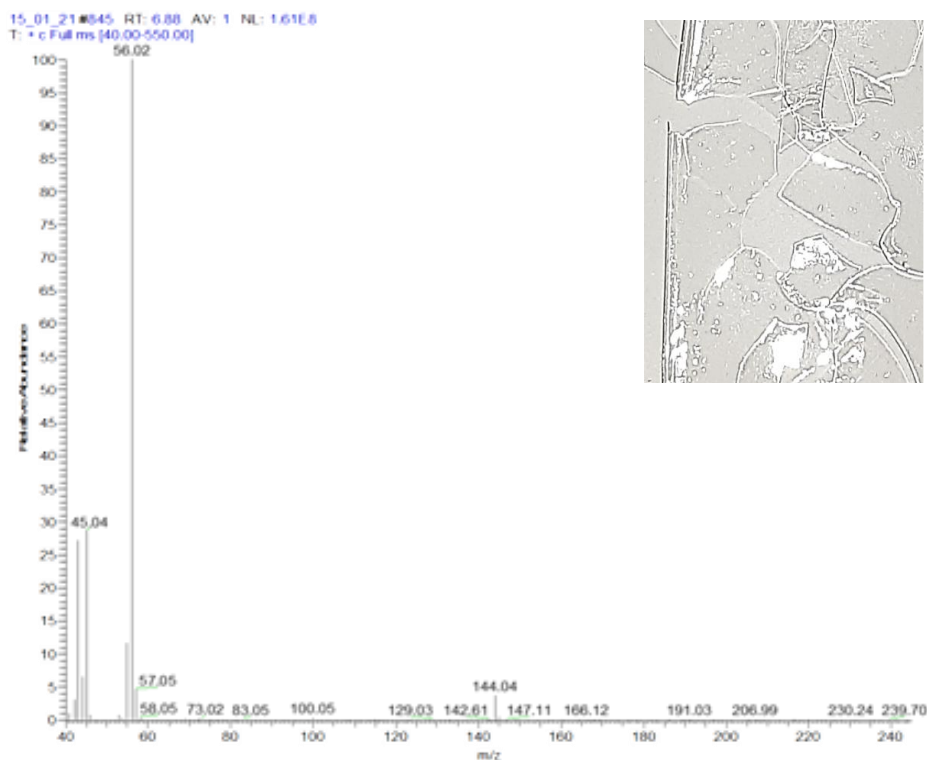
Fig. 2. Results of mass spectrometry, sample from pure polylactide after ultraviolet exposure
(in the insert of the figure)

The most intense series of peaks with values of the mass-to-charge ratio is observed in the range 45 − 56, which probably indicates the presence of lactide isomers in the decomposition products: meso-, D, or L. The obtained results of mass spectrometric analysis indicate the destruction of polylactide and the release of monomeric isomers of lactide.

The results of the change in the residual mass fraction for samples during decomposition at 60°C over time (more than 40 weeks) are presented in Figure 3.
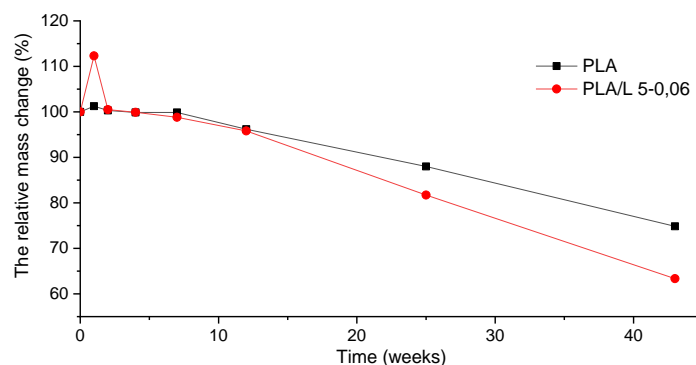

Fig. 3. Dependence the relative mass change of polylactide films on the hydrolysis time: 1 - without additives; 2 - addition of lignin 5%

The study of the hydrolytic degradation of the films shows that after thermostating for 43 weeks, weight loss, turbidity, poor extraction from water, and brittleness are

observed for all samples. The most destructible is the polylactide film without additives, and the most stable is the film modified with lignin.

3. Conclusion

Composite materials based on polylactide with lignin additives have been studied. The presence of the additive reduces the strength characteristics of films based on polylactide. However, the resistance to UV radiation of composites makes it possible to use lignin as an effective light stabilizer for polylactide films. Degradation of composites is characterized by the presence of the initial monomers of lactic acid in the decomposition products, and also has a degree of destruction in water comparable to the destruction of pure polylactide.

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