Development of a spatially structured polymeric matrix under UV irradiation of polylactide-based composites filled with aluminosilicate microspheres

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Abstract: *The relevance of the study is conditioned by the fact that increased consumption of synthetic polymers leads to an increase in environmental pollution due to the long decomposition time of plastic waste. As a result, it is necessary to develop polymer composites based on a biodegradable polymer matrix, and to improve the performance properties of finished plastic products, it is necessary to purposefully select cheap and affordable inorganic fillers. Thus, the purpose of this study is to investigate the regularities in the generation of a spatially structured polymer matrix under UV irradiation of polylactide-based composites filled with aluminosilicate microspheres (ASM). The leading approach to the given problem is to melt polymer composites of various compositions and to determine the physical, mechanical, and thermophysical characteristics of the prototypes, including the supermolecular structure of the polymer matrix under the influence of ultraviolet irradiation. The study suggests that the filling of polylactide with ASM particles leads to an increase in the elastic modulus, a decrease in the strength at static rupture and resistance to dynamic destructive effects, as well as heat resistance. Small aluminosilicate microspheres, when added to polylactide, perform the function of nucleation and, even with a small content, increase the crystallinity degree by 3.7 percentage points. In the range of ASM content from 1 pph to 10 pph, the absolute value of the crystallinity degree practically does not depend on the filler concentration in the polymer composite. UV (ultraviolet) irradiation in the presence of air oxygen initiates the thermooxidative destruction of polylactide and leads to the establishment of a spatially structured polymer phase using the electrostatic intermolecular interaction of additionally formed oxygen-containing functional groups in macrochains, as well as partial intermolecular crosslinking during recombination of macroradicals. The establishment of spatial structures in the polymer matrix under UV irradiation determines an increase in the resistance of experimental samples to thermal effects. It is manifested in an increase in the bending temperature under load by 7-10 percentage points, a decrease in the crystallinity degree by 1.2-2.6 percentage points, a decrease in the fluidity of the meltage and also an increase in the glass transition and melting temperature. The materials of the study are of practical value for the development of biodegradable composites based on polylactide filled with inorganic components.*

Key Words: *polylactide, aluminosilicate microsphere, breaking strength, crystallinity, impact strength*

1. INTRODUCTION

The steady increase in the consumption of synthetic polymers in everyday life and in production increases environmental impact due to the long period of decomposition of such materials. The key areas for solving this problem are the involvement of polymer waste in recycling, for which it is necessary to create an infrastructure for the collection and treatment of plastic waste, as well as to increase the share of consumption of biodegradable polymers. One of the most promising biodegradable polymers is polylactide (PLA), which is a product of lactic acid polymerisation.

The raw materials for the production of lactic acid are renewable resources, primarily corn and sugar cane.

Polylactide is a promising thermoplastic compostable polymer suitable for replacing synthetic polymers in the production of disposable tableware and packaging and for the manufacture of plastic products that require higher mechanical properties and stability to environmental factors (primarily ultraviolet). One of the ways to improve the performance properties of polylactide products is to fill it with inorganic components [1], [2], [3], [4], [5]. This study suggests the use of aluminosilicate microspheres (ASM) as a filler for the creation of polylactide-based polymer composites.

Hollow aluminosilicate microspheres are formed in the process of burning coal and have the form of hollow silicate spheres.

The elemental composition of ash microspheres is mainly represented by silicon (about 30% of weight) and aluminum (about 12% of weight) [6].

A successful combination of economic indicators with operational properties – the availability of resources (ash waste from thermal power plants), low cost and density, high strength and chemical resistance – allow the use of ash microspheres as fillers of composite materials, such as lightweight concrete, oil well cement, dry building mixes, refractory materials, polymer compounds [7], [8].

The structure of ASM determines the prospects for their use for the creation of polymer composites with the aim of [9], [10], [11], [12]: 1) increasing the mechanical strength and hardness of polymers; 2) reducing the cost of plastic products; 3) giving polymers special properties (reducing flammability, increasing friction or antifriction, electrical, thermal, adhesive, etc. characteristics).

The purpose of study was to investigate the regularities in the generation of a spatially structured polymer matrix under UV irradiation of polylactide-based composites filled with aluminosilicate microspheres.

2. MATERIALS AND METHODS

As a polymer binder, polylactide of the 4032D brand produced by Nature Works (USA) was used. The ASM consisted of ash in the form of hollow silicate spheres (with an average diameter of 136-147 microns) formed during the burning of coal.

The homogenisation of the polylactide meltage and ASM particles was carried out in the mixing chamber of the Plastograph EC (Brabender) at a temperature of 180°C, the screw rotation speed of 30 rpm for 15 minutes at a load of 200 N.

The content of ASM particles in the polymer composite was: 1, 5, 10 parts per hundred (pph) per 100 pph of polylactide.

The prototypes were obtained by injection moulding on a Babyplast 6/10P injection moulding machine at a temperature of 225°C, 235°C, 220°C, an injection pressure of 65 bar,

an injection rate of 30%, and a closing force of 35 bar. The temperature of the cooling water supply to the mould was 12°C, the mould holding time was 10s.

The prototypes, representing blades with a total length of 80 mm and a thickness of 2 mm in accordance with GOST 11262-80, were further subjected to UV irradiation and physical and mechanical tests.

Mechanical tests for uniaxial tension were performed in accordance with GOST 11262-2017 on a universal testing machine AGS-X10kN (Shimadzu) at a temperature of 23±2°C and a movable gripper speed of 1 mm/min to determine the elastic modulus, and a speed of 5 mm/min to determine other characteristics.

The microhardness of the surface of the studied samples was analysed by indenting on a dynamic microhardness meter DUH-211S (Shimadzu) according to GOST 9450 (method 2). The maximum loading force and the minimum loading after indentation – 196 mN and 1.96 mN, respectively.

The penetration depth of the indenter – 10 microns, the holding time after loading and before unloading – 5 s, the loading speed of the indenter – 35.0 mN/s. The method allows determining the microhardness of the surface according to Martens and the elastic modulus. The impact strength of the Sharpie samples (without incision) was determined according to GOST 4647-2015 on a GT-7045-HMH pendulum testing machine.

The bending temperature under load was evaluated in accordance with GOST 12021-2017 on a VICAT/HTD Tester. The melt flow index (MFI) of the compositions was determined on the Mi2 plastometer (Göttfert) according to GOST 11645-73 at 190°C and a load weight of 2.16 kg.

The thermophysical characteristics were studied by differential scanning calorimetry on a DSC 214 NETZSH Polyma (Netzsh) calorimeter in the temperature range of 30-200°C at a scanning speed of 10 deg/min.

The crystallinity degree of the polymer χ was calculated by the equation: $\chi = (\Delta H_i/\Delta H_o)\times 100\%$, where ΔH_i – specific heat of melting based on the content (i) of the polymer in the sample; DH_o = 93.6 J/g is the specific heat of melting of a completely crystalline polylactide.

For UV irradiation of polymer samples, a QUV (Q-Lab) weathering machine for accelerated ageing of materials was used. The studied samples were irradiated with UV radiation with a wavelength of 365 nm (radiation intensity 0.89 W^{m2}) at a temperature of 45°C for 25 days.

3. RESULTS AND DISCUSSIONS

Filling the PLA with ASM particles in a volume of 1 pph leads to a decrease in the elastic modulus from 3316 MPa to 3072 MPa (Table 1). Admittedly, this is conditioned by the loosening of the polylactide polymer matrix by ASM particles, which contributes to the production of a less rigid polymer sample.

Further increase in the ASM filling up to 5 pph and 10 pph consistently increases the elasticity modulus to 3465 and 3781 MPa, respectively.

The polylactide-based polymer composite with a high content of ASM particles is characterised by high rigidity, which allows producing overall plastic products on its basis [13], [14].

UV irradiation of pure PLA and a sample with a content of ASM particles of 1 pph for 10 days increases the elastic modulus by 20-25% compared to the initial samples. Further exposure to ultraviolet light leads to a slight decrease in the elastic modulus.

With an increase in the content of ASM particles in the polymer composite to 10 pph the elastic modulus reaches its maximum value during the irradiation process within the first 5 days. The analysis of the results of the surface indentation of polymer composites indicates that under UV irradiation for 5 days, the elastic modulus of the surface at the micro level decreases for all the considered samples (Table 1).

Thus, during the first 5 days of UV irradiation, the surface layer of the polymer sample is loosened, while the stiffness of the entire volume of the composite, observed upon break, increases [15], [16].

Table 1 – Physical and mechanical properties of polylactide filled with ASM particles

UV exposure, days	The ASM content, pph			
	0	1	5	10
Elastic modulus (rupture/indentation), MPa				
0	3316/ 3919	3072/ 4540	3465/ 3963	3781/ 4453
5	3726/ 2717	3462/ 3794	3980/ 3293	4487/ 2797
10	3993/ 4185	3824/ 4815	3864/ 2871	3993/ 4881
20	4038/ 4581	3404/ 4634	4094/ 4754	4038/ 4968
25	3478/ 2428	3620/ 4445	3900/ 3924	3914/ 4239
Elongation at break, %				
0	3.2	3.2	3.6	4.0
5	2.8	4.0	4.4	2.8
10	2.4	4.4	3.6	3.6
20	3.2	2.0	2.8	2.4
25	1.6	2.4	2.4	2.0
Charpy impact strength (without incision/with incision), kJ/m^2				
0	21.2/ 20.1	18.3/ 18.1	15.5/ 16.7	15.4/ 16.4
5	22.7/ 18.5	20.8/ 18.1	17.4/ 16.6	17.3/ 16.3
10	22.7/ 20.3	19.2/ 19.0	16.9/ 17.0	16.0/ 17.0
20	20.1/ 19.7	19.1/ 19.0	16.3/ 17.7	16.2/ 16.4
25	19.5/ 19.6	17.9/ 16.8	14.7/ 16.0	14.6/ 14.9
Bending temperature under load (1.8 MPa), °C				
0	55.2	53.3	51.7	50.6
5	58.7	58.8	58.4	59.1
10	59.7	59.7	59.9	59.6
20	60.8	61.9	61.3	61.4
25	62.0	61.2	62.2	60.3

The breaking strength of polymer composites consistently decreases with an increase in the degree of filling of the polymer with ASM particles (Figure 1).

Admittedly, this is conditioned by the presence in the volume of polymer sample of the phase interface of thermodynamically incompatible PLA and ASM particles, which reduces the strength of the polymer sample in the process of static tension.

The decrease in the strength characteristics of the polylactide during its filling with ASM particles determines the need for the use of compatibilisers that increase the affinity of the polymer phase and filler particles.

The decrease in the breaking strength during UV irradiation occurs only for a pure polymer, which may indicate that the ASM particles neutralise the effect of ultraviolet light on the polylactide. Similar changes occur when the polymer sample is dynamically exposed [17], [18], [19].

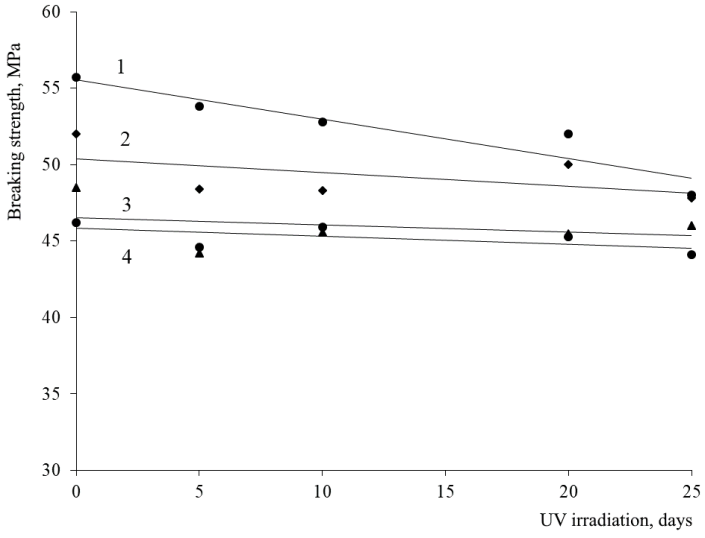

Fig. 1 – Dependence of the breaking strength of polymer composites on the duration of UV irradiation. The ASM content, pph: 0 (1), 1 (2), 5 (3), 10 (4)

With an increase in the degree of filling the PLA with ASM particles up to 5 pph there is a decrease in the Charpy impact strength, the value of which with further filling of the polymer composite up to 10 pph of ASM practically does not change (Table 1). UV irradiation during the first 5 days for all the considered polymer composites determines an average increase of 11% in the Charpy impact strength compared to samples not exposed to ultraviolet radiation. Admittedly, this is conditioned by an increase in the stiffness of the polymer composite, the quantitative indicator of which is the breaking strength (Table 1) [20]. The deterioration of the physical and mechanical properties of the polylactide during its filling with ASM particles is also observed when the polymer sample is exposed to heat. With an increase in the filler content to 10 m. h. there is a consistent decrease in the bending temperature under load from 55.2 deg for pure polylactide to 50.6 deg for the filled polymer composite (Table 1). The observed dependence allows predicting a decrease in the resistance of plastic products, manufactured from ALS-filled polylactide, to high temperature. UV irradiation of experimental samples for 5 days leads to an increase in load/deflection temperature by 6.3-16.7%, while the increased value correlates with the degree of filling of the polylactide with ASM particles (Table 1). During the further exposure of polymer samples to UV irradiation, the bending temperature under load increases slightly and practically does not depend on the degree of filling of the polylactide with ASM particles in the range from 1 pph to 10 pph [21], [22], [23]. The observed pattern can be explained by the course of thermal-oxidative degradation in the sample under the influence of UV irradiation, in which free radicals are formed, which increase the content of polar functional groups (peroxide and hydroxyl groups) in the macrocircuits in the presence of air oxygen. In addition, the possibility of intermolecular crosslinking during recombination of radicals formed in polylactide macromolecules under UV irradiation should not be excluded. The appearance of polar functional groups in the macrocircuit and the possible partial cross-linking of polylactide molecules leads to a decrease in their mobility, which determines an increase in the bending temperature of the polymer sample under load. This is confirmed by the change in the meltage fluidity of polymer composites. It can be seen (Figure 2) that the filling of the PLA with ASM particles is accompanied by an increase in the melt flow index over the entire range of the filler content.

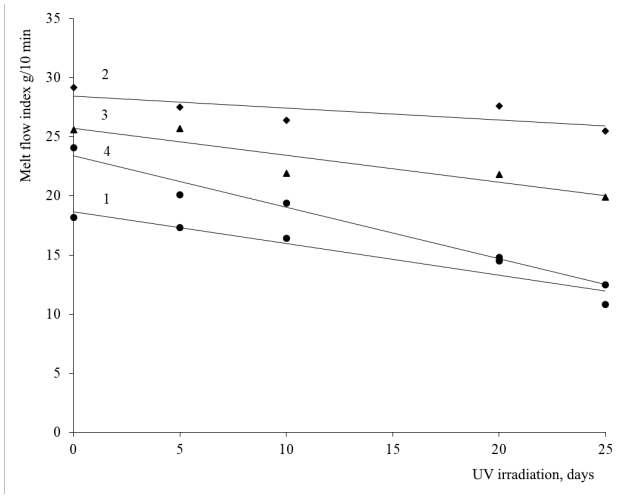

Fig. 2 – Dependence of the melt flow index of polymer composites on the duration of UV irradiation. The ASM content, pph: 0 (1), 1 (2), 5 (3), 10 (4)

Thus, the ASM particles, due to the destruction of the intermolecular electrostatic interaction of the polylactide polar macrocycles, make the polymer solution more fluid. Only when polylactide is filled with aluminosilicate microspheres above 10 pph, the fluidity of the composite meltage approaches that of a pure PLA meltage. For all the considered samples, UV irradiation is accompanied by a decrease in the MFI value, which may be associated with the generation of a spatially structured polymer matrix that reduces the meltage fluidity. This is confirmed by an increase in the glass transition temperature and the flow temperature of pure polylactide under UV irradiation (Figure 3). The low increase in the glass transition temperature (2°C) and fluidity (1.4°C) during the exposure of the polymer sample under UV irradiation for 25 days may indicate that spatially structured forms are developed not due to intermolecular crosslinking, but mainly due to the electrostatic interaction of functional groups in macro chains formed during thermal-oxidative destruction under the influence of UV light in the presence of air oxygen [24], [25].

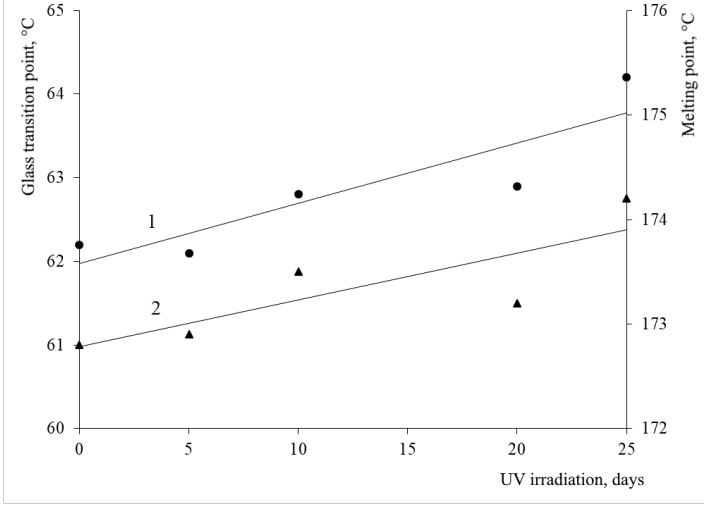

Fig. 3 – Dependence of the glass transition point (1) and the melting point (2) of the polylactide on the duration of UV irradiation

Analysis of the supermolecular structure of the polymer phase showed that ASM particles act as crystallisation centres that increase the crystallinity degree of the polylactide (Figure 4). The crystallinity degree of pure polylactide is 51.3%, which increases to 54.8%, 56.2% and 56.2%, respectively, when adding ASM particles in the amount of 1 pph, 5 pph, and 10 pph.

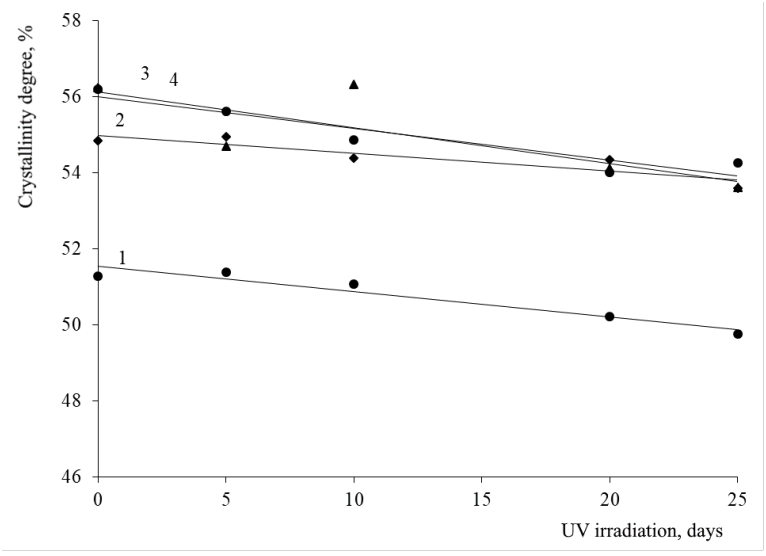

Fig. 4 – Dependence of the crystallinity degree of polylactide on the duration of UV irradiation. The ASM content, pph: 0 (1), 1 (2), 5 (3), 10 (4)

Figure 4 shows that the crystallinity degree of polylactide practically does not depend on the number of ASM particles introduced into the polymer composite. During the exposure of the polymer composite under UV irradiation for 25 days, the crystallinity degree decreases by an average of 3.3%, which is also conditioned by the generation of a spatially structured polymer matrix.

4. CONCLUSIONS

Filling of polylactide with ASM particles leads to an increase in the elastic modulus, a decrease in the strength at static rupture and resistance to dynamic destructive effects, as well as heat resistance. Small aluminosilicate microspheres, when added to polylactide, perform the function of nucleation and, even with a small content, increase the crystallinity degree by 3.7 percentage points. In the range of ASM content from 1 pph to 10 pph, the absolute value of the crystallinity degree practically does not depend on the filler concentration in the polymer composite. UV irradiation in the presence of air oxygen initiates the thermal-oxidative destruction of polylactide and leads to the establishment of a spatially structured polymer phase using the electrostatic intermolecular interaction of additionally formed oxygen-containing functional groups in the macrochains, as well as partial intermolecular crosslinking during recombination of macroradicals. The establishment of spatial structures in the polymer matrix under UV irradiation determines an increase in the resistance of experimental samples to thermal effects. It is manifested in an increase in the bending temperature under load by 7-10 percentage points, a decrease in the crystallinity degree by 1.2-2.6 percentage points, a decrease in the melt fluidity index, and also an increase in the glass transition and melting temperature.

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