Kinetics of biodegradation of strengthening polymer systems based on copolymers of lactic acid and biogenic activators

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Abstracts. The production of bioplastics based on copolymers of maleic anhydride with the addition of lactic acid and furyl alcohol is described. The obtained copolymers are promising for use as reinforcing polymer systems of cellulose-containing materials used in packaging. It has been shown that the use of lactic acid and furyl alcohol makes it possible to obtain synthetic bioplastics that are rapidly degradable in natural conditions, which is favorable for environmental protection.

1 Introduction

The development of science and technology in the field of polymers and polymer composite materials in recent years has been aimed at creating the latest composites with polymer inclusions that have a unique set of properties and combine a combination of strength and elasticity, thermal, chemical and light resistance, electrical conductivity, bacteriostaticity and others, which is practically absent in nature. characteristics [1].

The intensive development of polymer science has led today to a situation of impossibility of further safe use of synthetic polymers for mankind, since the volumes of produced and used plastics exceed the real possibilities of living nature to utilize this entire array of artificial materials created by man. A huge amount of slowly decomposing plastics in the environment is a serious environmental hazard [2, 3].

The main trend in the development of polymer science, which has been for all these years in the purposeful creation of durable polymer composites, has come into conflict with the safe use of advances in this field of science and technology. Obviously, the most important task today is the creation of such polymeric materials that would provide the whole range of properties during the period of operation, and then, being discarded, would quickly disintegrate into substances that do not pose a threat to nature and humans. The so-called bioplastics are precisely the representatives of a new generation of biocomposites. It is believed that such materials can be biodegradable if they have the ability to completely disintegrate in soil or water within six months [4, 5, 6].

The ideology of creating bioplastics is quite simple in comprehension and difficult in practical implementation. It is necessary to obtain a material with the desired properties, but

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having weak links in its polymer structure, which in the environment will be easily affected by natural enzymes and microflora available in an unlimited amount. That is, under favorable conditions for this, the polymer framework should decay in a controlled manner and rather quickly during hydrolysis with the formation of biogenic substances – activators favorable for active absorption by the microflora. The end products of decomposition must have low molecular weight compounds that do not pose a threat to wildlife, ideally, gaseous products [7, 8].

Any decomposition products of the composite and even the initial compounds themselves used to obtain the polymer can act as biogenic activators [9].

Packaging is significant in terms of the volume of use of polymeric materials. Taking into account the tendency to prohibit the use of disposable plastics in the food industry, already today in the European Union, the task of obtaining rapidly decomposing polymeric materials in nature is becoming more and more urgent [10, 11]. Large-scale use of traditional paper raw materials for these purposes is becoming a development trend and is limited only by the insufficient strength of paper products.

Analysis of the quality of paper in the Russian market shows that it is mainly made from softwood sulphate unbleached pulp and semi-kraft pulp. Most of these types of paper are not produced at Russian factories, as evidenced by the nature of the formation and distribution of fibers in the paper sheet. In the mass of the paper composite, there is a fairly fine grinding with a high degree of fibrillation of the fibers with maximum retention of their length and paper-forming properties. Such paper is produced from raw materials that have passed 3–4 processing cycles. The presence of a certain amount of long-fiber and well-fibrillated fraction indicates the addition of up to a third of secondary raw materials to the raw material, which is quite sufficient for the production of paper [12, 13].

As the analysis shows, secondary fibrous raw materials, passing, in particular in European countries, multiple, up to 15 or more processing cycles, is a material consisting of short non-strengthening cellulose fibers with a low crushing ability and very low paper-forming properties, which in first of all, it affects the insufficient strength of the paper product [14, 15, 16]. The application of a polymer hardening coating to the paper surface makes it possible to obtain a biocomposite with improved properties. Naturally, in accordance with today's requirements, the applied coating should promote rapid biodegradation.

The aim of the work is to obtain a biodegradable polymer material for modifying the properties of cellulose-containing materials and to study the kinetics of its degradation in natural environmental conditions.

2 Materials and methods

2.1 Raw materials

As objects of research, we used monomers to obtain a polycomposite: maleic anhydride, glycerin, furfuryl alcohol, and lactic acid of p.p.a. qualification Serva (Germany).

2.2 Methods

The block copolymer was obtained by the polycondensation method. Glycerol and phthalic anhydride were used in a 2:3 molar ratio in accordance with the number of reactive functional groups. The amount of lactic acid added was 10% of the amount of phthalic anhydride. The reaction mixture was added 1% of the mass. furyl alcohol.

The reaction for obtaining the modified polymer was carried out at a temperature of 160 °C for 1.5 hours. The control of the polycondensation process during the synthesis was

carried out by the acid number (**AN**), defined as the number of milligrams of potassium hydroxide required to neutralize the free carboxyl groups contained in one gram of the substance [17].

The tensile strength of polymer film systems under tension on a paper base was studied using an Instron 3369 tensile machine (USA) according to the standard method [18]. The width of the biocoated paper test specimens was 15 ± 0.2 mm, the length was 250 mm. Used paper samples with a density of 50 – 80 g / m^2 and a thickness of 0.07 to 0.1 mm.

The hydrolytic stability of the obtained bioplastic in the environment was studied by molding tablets by pressing a homogeneous mixture of podzolic soil with a copolymer (1: 1) 5 cm in diameter, 2 cm thick and placed in forest soil to a depth of 20 cm.The tablets were removed from the soil with a time interval of 14 days. and analyzed the state of the material (appearance, geometric shape, weight).

3 Results and discussion

Glyphthalic polymers are the most common types of polyester alkyd resins, and are products of the polycondensation of glycerol and phthalic anhydride. Modified glyphthalic copolymers are used mainly in the form of film coatings to protect various unstable decorative patterns and surfaces, in particular, in the woodworking industry [19].

To obtain strengthening polymer systems capable of accelerated biodegradation, block copolymers were synthesized containing residual units of o-phthalic acid, glycerol, lactic acid, and furfural. It was assumed that lactic acid molecules can enter into an esterification reaction not only through the carboxyl group when interacting with glycerol hydroxyls, but also interact through an alcoholic hydroxyl with carboxyl groups formed in the first stage of the reaction from phthalic acid anhydride. In addition, the interaction of lactic acid molecules with each other is possible with the formation of both lactide and polylactide. The presence of residual furfural units in the polymer can contribute to its biodegradation [20, 21].

To compare the processes occurring during the synthesis of unmodified lactic acid and the modified product, the unmodified polymer was synthesized under the same conditions. At the same time, it was noted that the decrease in the acid number with the introduction of the modifier occurs faster, as shown in Fig. 1, in spite of the fact that the proportion of the acidic component with the introduction of lactic acid is higher. The resulting ratio of carboxyl groups and alcohol hydroxyl groups in this case is 4:3. Whereas when receiving an unmodified alkyd resin, this ratio is 3:2. The lower value of the activation energy of the reaction for the formation of polylactide from lactic acid (70.9 kJ/mol), in comparison with the activation energy of the reaction of the interaction of glycerol with phthalic anhydride (79.5 kJ/mol), suggests a higher chemical activity of lactic acid in the studied synthesis, as well as the possibility of its participation in the formation of a polymer with a cross-linked three-dimensional structure [22].

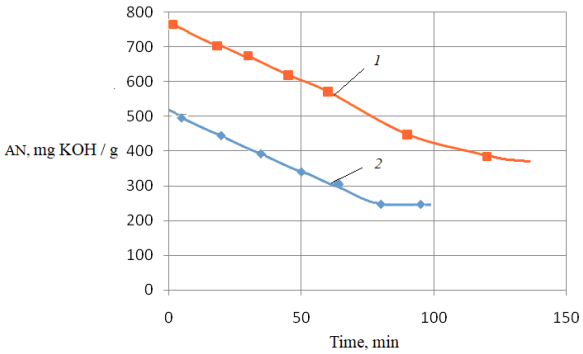

Fig. 1. Dependence of the acid number AN on the synthesis time: 1 – unmodified; 2 – modified copolymer.

Tables 1 and 2 present data on the physical and mechanical properties of biocomposites obtained on the basis of paper of various densities with surface application of a modified and unmodified copolymer. From the presented data, it can be seen that the surface treatment of paper samples led to their strengthening by 20–45%, depending on the treatment. In all cases, the application of an equivalent polymer layer to the cellulose-containing surface resulted in its hardening.

The strength of the treated materials increased in comparison with the initial samples, since the surface treatment leads to the hardening of the material structure. When visually examining the sample sections under a microscope, it was noticeable that the darkened or whitened, depending on the amount of application, the surface layer of the paper pulp impregnated with the copolymer had a greater thickness. The effect of enhancing the strength properties of high-density paper samples is apparently associated with the greater longitudinal orientations of the fibers during the technological production of the paper base. Since paper is a more porous material, it is evident that impregnation has a similar strength-enhancing effect.

Glyphthal resin has a yellowish tint, and the resulting modified resin is darker, brown in color, which must be taken into account later when using the modified polymer as biodegradable polymer films.

Table 1. Tensile tensile strength along the grain of processed and untreated types of paper, MPa (n = 10).

Name	Initial sample	Superficial treatment glyphthalic copolymer based on glycerin and maleic anhydride	Treatment modified copolymer with lactic acid and furfuryl alcohol
Paper, density 50 g / m^2	13	16	17
Kraft paper, 80 g / m^2	16	18	23

Tests of the obtained products for decomposition in the soil layer showed the following. Formed samples from unmodified and modified polymers had different degradation rates. On average, copolymers with additives of lactic acid and furyl alcohol lost 5–9% in weight per week. By the end of the third month, the tableted samples were completely degraded and it was impossible to distinguish them from the surrounding soil. The polymer component turned into a loose, porous mass, which, even under a microscope, could hardly be separated from the surrounding soil.

Table 2. Tensile strength at tensile across the fibers of processed and untreated types of paper, MPa (n = 12).

Name	Initial sample	Superficial treatment glyphthalic copolymer based on glycerin and maleic anhydride	Treatment modified copolymer with lactic acid and furfuryl alcohol
Paper, density 50 g / m^2	12	14	15
Kraft paper, 80 g / m^2	15	17	20

The kinetic equation of polymer decomposition, according to gravimetric data, corresponded to the kinetic equation of the first order, however, the degradation rate constants were not reliably determined due to significant seasonal temperature fluctuations with the transition from spring to summer.

Similarly, tablets made from unmodified glyphthalic copolymer based on glycerol and maleic anhydride showed significantly greater resistance to storage in soil. The rate of their degradation was significantly lower, and even after 9 months. the tableted samples retained their original shape and had a weight loss of no more than 10%. In vivo storage tests were discontinued due to the onset of winter.

4 Conclusions

Thus, the introduction of lactic acid as a modifier makes it possible to reduce the polyester synthesis time. The obtained polyesters can be used for surface hardening of cellulose-containing materials. The materials are relatively safe from the point of view of their rapid degradation in the environment. This work can be considered as an approach to the development of an effective methodology for the production of environmentally friendly bioplastics.

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