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BIODEGRADABLE POLYMER COMPOSITES MATERIALS BASED ON SYNTHETIC POLYMERS AND NATURAL COMPONENTS

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The study aims to create biodegradable composite materials based on non-emulsion polymer latexes with natural fillers. The article provides an analysis of the current status of the issue on the methods of obtaining biodegradable polymer materials and methods for confirming their biodegradation under the influence of biotic and abiotic factors. The results of research on the development of a method for obtaining biodegradable polymer materials based on based on 1,4-cis-polyisoprene non-emulsion polymer latexes are presented. Using the method of determining the degree of decomposition of polymers under simulated composting conditions in laboratory tests, the ability of the created polymer composite products to biodegradation under the influence of soil microbiota has been proved. Stimulation of biodegradation processes occurs due to the natural fillers of wood flour and coffee oil cake introduced at the latex stage in the form of pre-prepared suspensions. The developed technology makes it possible to obtain, using the method of coagulant sedimentation, composite polymer thin-film materials with adjustable operating time, makes it possible to reduce the load on the environment after the disposal of used products by burying them into the soil at polygons. The obtained polymer composite materials can be used to obtain dipped articles, for example, gloves for household, pharmaceutical, and chemical purposes.

Introduction

Synthetic polymers are widely used in medical, household, chemical, pharmaceutical, engineering, and other industries. Gloves, packaging materials, and disposable medical devices have a short life cycle, often less than one month, and sometimes are single use. As of 2018, more than 3 million tons of plastic waste was generated in Russia alone, and only 12% of it was sent for recycling, with the materials partially losing their original mechanical properties. Due to this, the number of landfills full with solid polymer waste increases every year. One of the reasons for the rapid growth of plastic waste is how difficult it is to make synthetic polymers decompose naturally; for example, they are not processed by microorganisms due to their high molecular weight or resistant to environmental factors (water, light, temperature) due to cross-linking between macromolecules or the composite structure of products [1-5].

In recent years, a new approach to the development of plastics has emerged. The aim of this approach is to obtain polymers that would retain their performance characteristics only during the period of consumption, and then undergo physical, chemical, and biological transformations under the influence of environmental factors and included in the metabolic processes of natural systems. The development of biodegradable polymer materials could be a step towards solving the global environmental problem of waste disposal.

Today, many companies around the world produce biodegradable plastics. For example, ICI (Great Britain) has created new industrial polymeric materials produced with bacteria on natural substrates. The polymer poly-3-hydroxybutyrate synthesized by bacteria is the basis of Biopol composite material used in the food industry for packaging.

In Russia, the production of biodegradable polymers is not a large market, and import of such materials is expensive for manufacturers of products made of them. Therefore, these products (packaging, gloves, medical products) are expensive and not widespread in Russia. This is why the development and manufacture of biodegradable materials is relevant and promising for other industries [6].

Currently, there are different approaches to create biodegradable plastics. For example, there is the selection of special strains of microorganisms that degrade polymers or the synthesis of biodegradable polymers that have a chemical structure similar to that of natural polymers. In addition to these methods, it is possible to create compositions based on high-molecular compounds, which include various natural fillers that contribute to decomposition by microorganisms. Polysaccharides, such as starch, cellulose, and protein-containing substances are widely used as such fillers. Such modification allows not only to reduce the production cost of the final product, but also to improve some technological properties of products. Usually, the manufacturers do not use these fillers in their pure form, but as wastes from other industries [7].

Money is the most important factor of any production. Considering that waste can be a natural filler, the production of biodegradable composites saves a lot of money on procuring it. For example, one such waste is coffee press cake, which is a constant by-product of various catering organizations. Another large-volume waste is by-product of wood processing, which is wood powder. It is suitable as a filler due to its high degree of dispersion. Let us consider in more detail the feasibility of using the above-mentioned wastes for industrial production of biodegradable composite polymeric materials.

Wood powder is small particles of hardwood or coniferous trees. Wood powder particles include cellulose, lignin, and pentosans. The high thermal resistance of wood powder (thermal destruction begins at 275-285 °C) enables its processing into composites by standard methods. Due to the content of cellulose and lignin in wood powder, it is prone to biodegradation due to enzymatic oxidation by fungi (peroxidase, laccase). In 2012, the volume of wood powder production amounted to 205.7 thousand m^3, and the cost per kilogram was estimated at 0.22-0.39 USD.

Coffee press cake contains 20% cellulose and hemicellulose, pectin, lignin, microelements, and proteins. Coffee press cake has a high thermal degradation temperature (about 285 °C), which also makes it possible to use standard methods in the manufacture of composite materials. The biodegradability of coffee press cake is due to cellulose in its contents, as well as microelements and proteins, and the mechanism of biodegradation is similar to that of wood powder [8-13].

The main advantages of biodegradable polymers: they can be processed with standard equipment; they can be used for the production of packaging materials, including food packaging; waste can be easily disposed because it can decompose under natural conditions.

From a market perspective, the growth prospects for the consumption of biodegradable polymers are significant. There is a market niche, new profitable enterprises, the properties of new biopolymers are getting closer to the traditional polymeric materials such as polystyrene, polypropylene, etc. Now more than 30 different biopolymers are available. They are widely used not only in the packaging market, but also in the textile industry, agriculture, medicine, and construction. Almost all major manufacturers of plastics offer their own biodegradable materials [14].

The project proposed by the joint venture of the two largest companies in their segments – agricultural giant Cargill and chemical leader Dow Chemical – is considered the most successful. This venture, which is called Cargill Dow, claims to be the leader in the production of polylactic acid (PLA), a polymer made from plant sugars from renewable agricultural resources: grains and sugar beets. Intended applications are biaxially oriented packaging films, rigid containers, and even coatings. The company claims that PLA polymer packaging can fully decompose within 45 days, provided an appropriate composting structure is in place. It should be noted that unlike its competitors, Cargill Dow's biopolymers have been quite successful commercially. Their success is confirmed by the interest of Hoechst TrespaphanGmbh in them, a renowned manufacturer of oriented films.

Synthesis of specific polyethers and polyetheramides is the priority direction of biodegradable synthetic plastics production nowadays. Two chemical giants, BASF and BAYER AG, are particularly active in this regard. Degradable copolyethers are obtained from aliphatic diols and organic dicarboxylic acids. It was found that their tendency to biodegradation depends on the amount of terephthalic acid in ester in relation to aliphatic acid and is 30-55% mol. Based on this polyester, BASF produced the fully biodegradable plastic Ecoflex F as far back as 1995. It is used in sacks, agricultural films, sanitary films, and laminating paper. The mechanical properties of Ecoflex F are comparable to low density polyethylene. Using this, the company produces a film with high tensile strength, flexibility, water resistance, and water vapor permeability.

BASF has also mastered the production of biodegradable plastics based on polyesters and starch. Since the second half of 90-s, BAYER AG produces new compostable aerobic biodegradable thermoplastics BAK-1095 and BAK-2195 based on polyesteramide. This material has high adhesion to paper, which allows its wide use for the manufacture of moisture- and weather-resistant packaging used in the food industry and in agriculture. With appropriate hydration, BAC-1095 bags decompose in compost into biomass, carbon dioxide and water in 10 days.

Unfortunately, insufficient attention is paid to the development and practical implementation of biodegradable plastics in the Russian Federation. At the same time, it should be noted that there are companies in Russia that produce biodegradable packaging as well. One of the first Russian companies to produce biodegradable polymers is Eurobalt, St. Petersburg. Dar, Tikoplastic, Artiplast, Murmanskplast, Biaxplen manufacture similar products. Unfortunately, these are still isolated offers in the Russian market of biodegradable packaging materials [15, 16].

Biodegradable polymers and materials should be partially or completely degradable to mineral (inorganic) components without producing any environmentally harmful substances. This definition includes not only the degree of biodegradation, but also the decomposition of the polymer by the environment and microorganisms into compostable substances that are non-toxic to humans.

Thus, biodegradation is associated with the decomposition of organic polymer into low molecular weight substances and its mineralization, with the loss of all its original chemical and physical properties. The end products of decomposition are environmentally and human friendly substances [17-19].

To study the biodegradability, various methods are currently used to evaluate biodegradable polymeric materials: fungus resistance test, burial test, composting simulation in a laboratory to determine the degree of plastics decomposition, evaluation of full aerobic biodegradability and decomposition under controlled composting conditions, carbon dioxide emission analysis [20-22].

Study

This study uses an artificial latex of cis-1,4-polyisoprene (SKI-3) to create a polymer basis for the composite material. Films based on this latex have good gas and vapor tightness and hypoallergenic properties.

The first stage in manufacture of dipped products is production of artificial latex. It is essentially preparation of an organic solution of synthetic rubber followed by its emulsification with solutions of surfactants and vacuum distillation of the solvent to form an aqueous dispersion of the polymer. To prepare the emulsion, a freshly prepared sodium caseinate solution and water are added to the emulsion machine tank, and SKI-3 solution is slowly added in when the machine is turned on. The emulsification process continues until a stable milk-colored emulsion is formed. At the first stage, the solvent is distilled from the obtained emulsion at atmospheric pressure in the presence of nitrogen, enough to reduce the amount of coagulum formed. At the second stage, the obtained latex is concentrated under vacuum [23, p. 280].

Natural fillers are added for the biodegradable properties to the polymer product. These fillers include wood powder, various dispersed fractions, and coffee press cake.

The latex composition for the manufacture of dipped products is prepared by sequentially introducing the following ingredients into the concentrated SKI-3 latex: non-ionic emulsifier OP-10 (for additional stabilization), dispersion of sulfur, zinc oxide, zinc diethyldithiocarbamate, sodium diethyldithiocarbamate solution. They represent the curing system, as well as dispersion of natural filler to secure biodegradation of the composite material. The components are slowly stirred in the latex composition, then it is left alone to mature.

Coagulant deposition is used to create polymer films. This method requires coagulant solution. The research showed that an aqueous solution of calcium chloride is the perfect candidate as a coagulant to coat the dipping forms uniformly and help to easily remove the products off the molds [23, p. 281].

During the process, the dipping molds are cleaned and dried. Porcelain molds with a smooth, glazed surface were chosen to create the films, which also makes it easier to remove them off the molds.

The molds are immersed in the coagulant evenly, smoothly, and slowly enough so as to leave any air bubbles outside. The most acceptable immersion rate was determined to be 0.6-1 cm/s. The extraction rate of molds from the aqueous coagulant was chosen to be within 0.5 cm/s.

The molds are then smoothly dipped in the prepared latex composition. The convex shape of the meniscus between the latex composition and the mold can be used to assess if the speed fits the process. In this study, the immersion rate was 1.5-3 cm/s. The mold soaking time in latex composition was determined by the required thickness of the product and was selected experimentally for specific conditions. In order to avoid prolonged soaking of the mold in the latex composition, it is dipped several times. The mold is repeatedly immersed into the coagulant and then back into the latex composition. With this method, the choice of drying time of latex gel and coagulant before re-immersion is very important. A mistake at this stage can lead to the product breaking.

The molds are slowly extracted from the latex composition to ensure that the excess latex composition is removed during the lifting process. The recommended extraction rate is 0.5-1 cm/s. After removing the mold, the excess composition should be allowed to drain off, and the mold is then slowly rotated at a specific speed (6 rpm) to distribute the latex gel evenly over the surface. It is then dried in a convection dryer by feeding warm air until the moisture is completely absent.

After the films are dried, the product is cured at 130-140 ℃. The final stages are washing the obtained products from non-rubber substances and removing the product from the mold. To wash the mold, it is dipped in distilled water along with the product for 30 minutes. The highest efficiency was achieved by increasing the frequency of water changes. The films are then removed from the molds by hand.

We obtained samples of polymeric films of synthetic isoprene rubber (SKI-3) in a similar manner. They have potential biodegradability with two types of fillers, wood powder and coffee press cake.

In order to confirm the possibility of biodegradation of the obtained samples of composite polymeric material, we conducted tests in accordance with ISO 20200:2015 (GOST R 57225-2016).

As a result of the study, we obtained the dependencies of the degree of biodegradation D on time *t* (Fig. 1, 2).

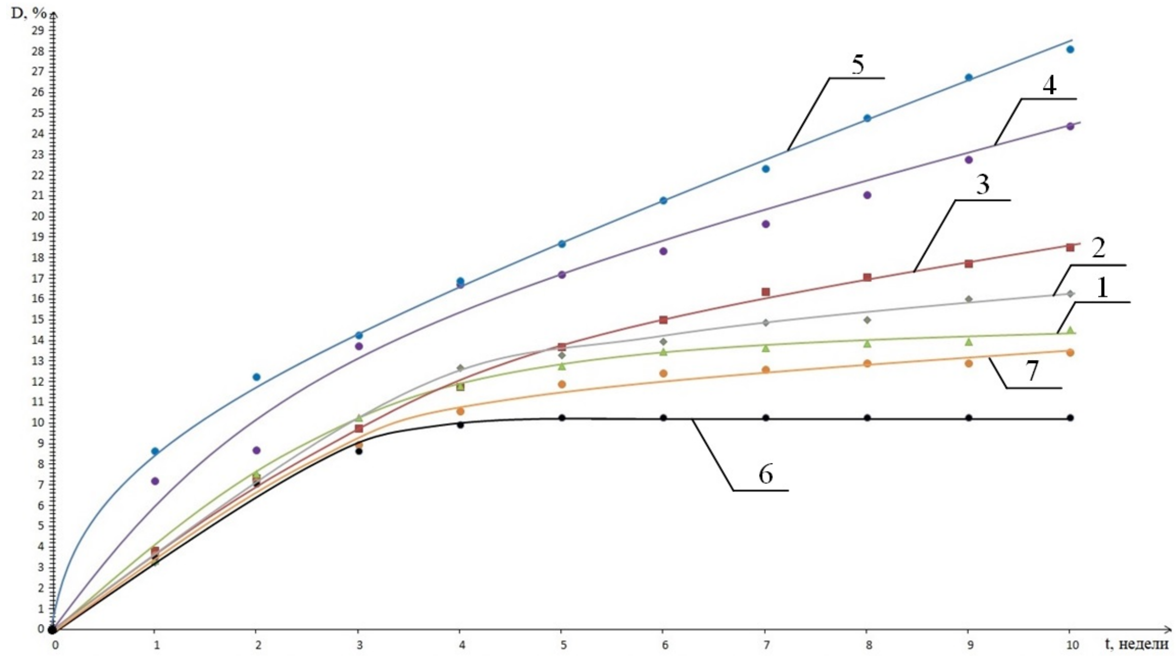

Fig. 1. Polymer films biodegradation to composting time dependence graph films based on SKI-3, filler – wood powder, fraction 200 microns: 1. 5 m/v; 2. 10 m/v; 3. 15 m/v; 4. 20 m/v; 5. 25 m/v; fraction 400 micron: 6. 2.5 m/v; 7. 5 m/v

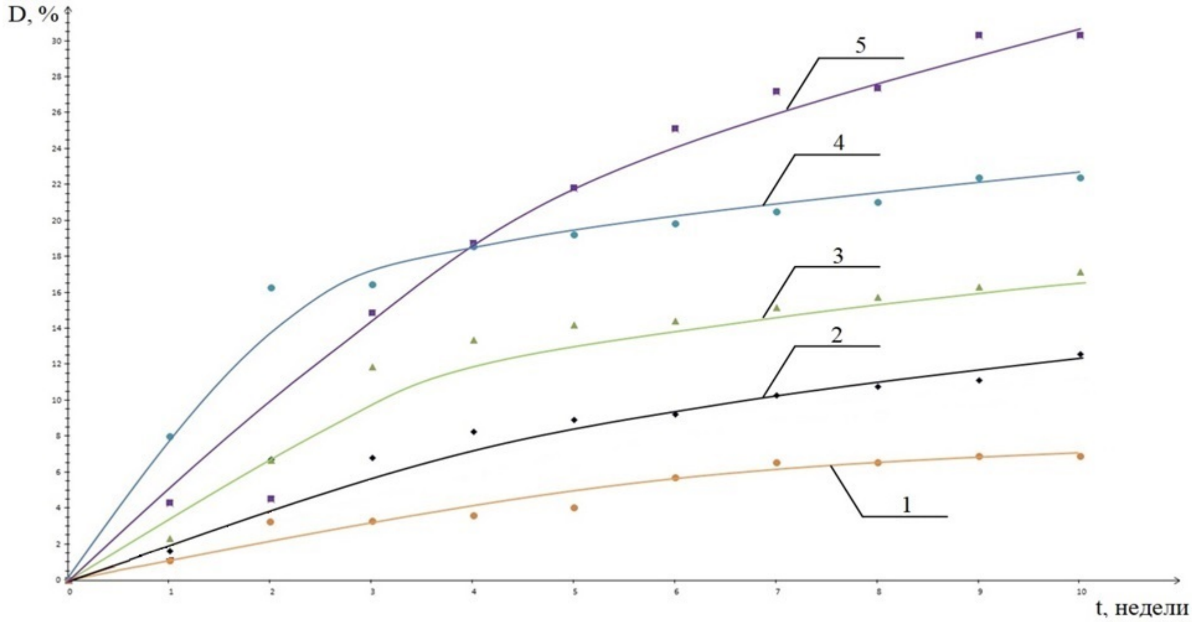

Fig. 2. Polymer films biodegradation to composting time dependence graph 1. SKI-3, no filler; 2. SKI-3, filler – coffee press cake: 2. 5 m/v; 3. 10 m/v; 4. 15 m/v; 5. 20 m/v

As the number of natural components increased, the degree of biodegradation also increased, and after introducing a more highly dispersed filler over the period of the experiment, the process was more intense. Coffee press cake was a better biodegradation stimulator compared to wood powder, apparently due to the presence of protein compounds in its composition. The polymer films fragmented into 2-10 mm particles during the tests, and we could not conduct further tests for this reason.

Conclusion

As a result, the study shows the potential biodegradability of the samples of the developed composite polymeric material based on synthetic polymers and natural fillers. Another result is the method of production and contents of a latex composition to manufacture thin-film dipped products containing natural fillers, which were introduced at the latex stage.

The study is highly relevant for Russia due to a small range of such products. Increasing the use of biodegradable polymeric products in the production of packaging materials, medical and household items can be one of the promising ways to solve the environmental problem of the ever-increasing volume of polymer waste.

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