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BRIEF COMMUNICATIONS

Biodegradable Composite of Starch and Carboxylated Latex for Arts and Crafts

E. A. Polyakova, I. S. Korotneva, B. S. Turov, A. S. Danilova, and A. V. Komin

Yaroslavl State Technical University, Moskovskii pr. 88, Yaroslavl, 150023 Russia
e-mail: elizaveta.ponomareva.91@mail.ru

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Abstract—A biodegradable composite of starch and latex of carboxylated methyl methacrylate-butadiene copolymer for decorative and applied art was developed and its performance was studied. The composite degrades in the environment after the end of the service life.

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Polymeric materials with controllable composition and unlimited variety of properties are increasingly used in various fields of industry and in homes. However, owing to increasing production volumes, formation of a huge amount of plastic waste and its disposal is the major environmental problem. Therefore, the development of composite polymeric materials with a controllable service life, which retain performance during consumption and then degrade in the environment to form non-toxic substances, is the urgent problem.

One of promising ways in development of such materials is a combination of synthetic polymers and natural polymers, providing degradation of the total composition. The most commonly used natural biodegradable component is starch. This is because it is available and non-toxic material and natural resources for its production are inexhaustible [1–5].

Currently, one of important directions is the development and preparation of materials for arts and crafts, which are plastic during the manufacturing articles and then harden in air without additional treatment. Despite the growing demand, synthesis of such materials in Russia is almost absent. Consequently, the development of new biodegradable self-hardening composites is the urgent problem for import substitution and reduction of environmental load.

The goal of the study is the development and preparation of a non-toxic, environmentally friendly biodegradable composite material based on natural and synthetic polymers for arts and crafts. The biodegradability of new composite under the environmental conditions was determined.

EXPERIMENTAL

As filler for new polymeric composite, we used high molecular weight polysaccharide, potato starch (75 wt %), which is highly biodegradable and accessible material (Garnets, Russia). As a polymeric matrix were used synthetic latexes of carboxylated butadiene-methyl methacrylate copolymers (20 wt %) synthesized by the heterophase emulsion polymerization by the previously developed technology [6]. To increase thermodynamic compatibility of the components and improve plastic properties of the composite, glycerol (0.7 wt %) from the Ekros Joint-Stock Company (Russia) and castor oil (4 wt %) from the Tula pharmaceutical plant (Russia) were introduced as plasticizers, the latter being also a prooxidant that increases biodegradability of the composite.

Polymeric composition in the form of a plastic white pasty mass was prepared by mechanical stirring of the above components for 5 min under natural conditions. The resulting product is a homogeneous soft material that does not stick to hands, retains its shape in the manufacture of parts of varied size and thickness, and does not crack during molding and after hardening. The viability time

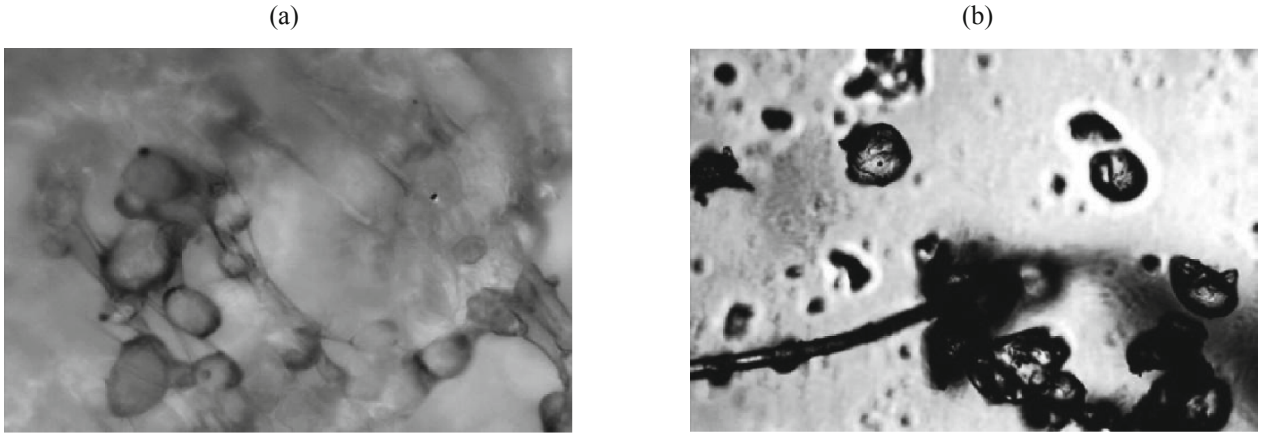

Fig. 1 Micrographs of the sample (a) before and (b) after the exposure to UV radiation. Magnification ×640.

of the material (during which plastic properties in air are retained) is 40-45 min. Plastic mass is stored in hermetically packaged gas-tight container. The finished product is completely solidified in air at room temperature for 10–24 h. Samples of the composite in the form of a cube were successfully withstood the dropping, impact, and dipping tests by GOST (State Standard) 51555-99. The destruction degree of the samples did not exceed 0.01%, showing that the use of the composite for arts and crafts is effective.

To determine, if a polymeric composite may be transported in a climate of Russia, we studied its ability to withstand multiple cycles of freezing (from –15 to –20° C) and following thawing (at 15–20°C). It was established that the composite material does not lose performance after 15 cycles of testing.

The biodegradation ability of the new composite material after the end of the service life was determined under the conditions modeling the environmental factors, including UV irradiation and the presence of micromycetes and soil microorganisms**.**

The effect of exposure to UV radiation with a wavelength of 290–320 nm on samples of the new polymeric composite was determined at 28°C and a 50–60% humidity for 320 h. It was found that the sample color changes from white to yellow, which indicates aging of the material. Figure 1 demonstrates the micrographs of the samples (a) before and (b) after the exposure to UV irradiation (Altami BIO-2 biomicroscope). The microscopic study showed that the starch grains became rough around the edges and cracked. Threads of a polymeric binder became longer and thinner and their number also decreased compared to initial material.

To determine the biodegradability of a material under the action of micromycetes, mold cultures were grown on samples of the polymeric composite and incubated. Infected samples were kept in a desiccator at relative humidity of 100% and temperature of 28 ± 1°C for 28 days. It was established that, owing to abundant biofouling, zygomycotes, micromycetes (*Mucor sp.*), and mitosporic ascomycotes (*Aureobasidium, Acremonium, and Sladosporium*) ensure biodegradation of the material. To confirm biodegradation of the polymer composite, we compared the deformation and mechanical characteristics of the material before and after the exposure to *Mucor micromycetes*. The measurements were performed on an ITS 8220-10 tensile testing machine (Ivanovo) at extension 10 mm min^{-1}. The obtained $\sigma = f(\varepsilon)$ dependences of mechanical stress on the relative elongation were used to determine the tensile strength, Young modulus, and rela-

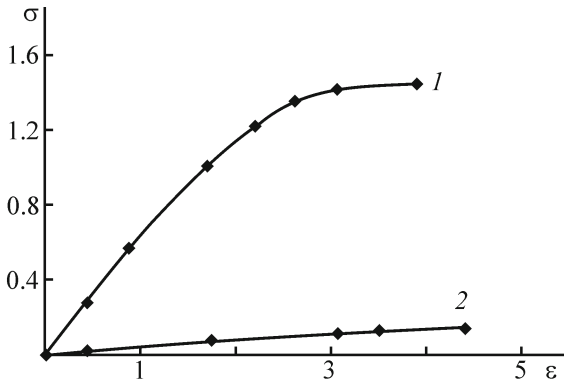

Fig. 2. The $\sigma = f(\varepsilon)$ dependence (*1*) before and (*2*) after the exposure of the material to micromycetes (*Micor sp.*) (σ) Mechanical stress (MPa) and (ε) relative elongation (%).

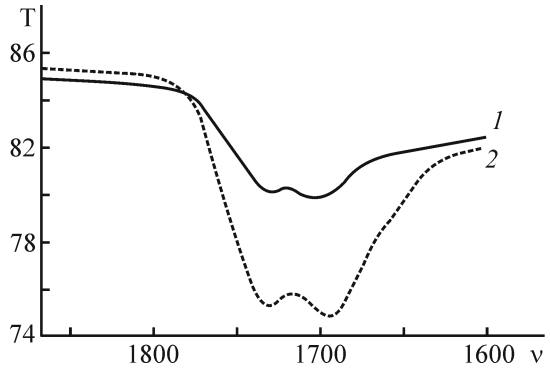

Fig. 3. IR spectra of the material (*1*) before and (*2*) after the exposure to soil microorganisms. (T) Transmission and (ν) wave number (cm^{-1}).

tive elongation of the samples (Fig. 2, Table 1). After the exposure to micromycetes, the strength of the material decreased by 90%.

Composite samples were incubated in sod-podzolic loam soil at a temperature of 20 ± 1°C and a relative humidity of 80 ± 2% for 3 months. The structure of the composite under the influence of soil microbiota was determined after equal intervals of time and the regular changes were found. The first stage of the process is active absorption of water and wash out of a part of filler from the polymeric matrix of the composite, which makes it more accessible to microorganisms and assists subsequent biotransformation.

The second stage is adhesion of bacteria to the surface of the material, the penetration of microscopic micellial fungi inside the polymer composite, and the use of bioaccessible filler as nutrition source. In a process, a color of the composites changes, a layered structure appears, and a significant loss of strength takes place. As known [7], the primary condition for the biodegradation of polymers in vivo is their oxidation with the formation of hydrophilic functional groups.

Deformation and mechanical characteristics of the materials

Sample	Tensile strength, MPa	Young modulus, MPa	Relative elongation, %
Material:			
Before exposure to micromycetes	1.360	70.56	2.7
After exposure to micromycetes	0.077	4.44	5.6

During the exposure of microorganisms to the composite material, the proceeding of irreversible oxidation reactions was recorded at the third stage of the process. To do this, we measured intensity of the absorption bands of the carbonyl groups in the range of 1800–1650 cm^{-1} [RX-1 FTIR spectrophotometer (Perkin Elmer)]. Figure 3 demonstrates IR spectra of the samples before and after the exposure to microorganisms (curves *1* and *2*, respectively).

It was established that the amount of carbonyl groups in the sample exposed to microorganisms sharply increases, which may be due to oxidation of hydroxyl groups of the starch. Also, we should not exclude that the accumulation of metabolic products of soil microorganisms formed by biochemical transformations in the composite and the disruption of polymer chain by acrylic fragment, may cause growth of the carbonyl groups. The further course of the process leads to a fragmentation of the polymeric composite and subsequent mineralization.

Toxicity of the composite material was tested using radish as indicator plant, because its seeds have a high response to toxic substances. Plant growth was monitored during 1 month in the initial soil (reference sample) and in the soil containing 10 g m^{-3} of polymeric composite, which is much higher than the commonly used concentrations for evaluating soil toxicity. The bioindication (GOST 12038–84, GOST 17.4.1.02–83) showed that the polymeric composite does not adversely affect the growth of plants, which confirms the safety of its utilization on burial in soil.

CONCLUSIONS

(1) Polymeric composite based on synthetic latex of carboxylated butadiene-methyl methacrylate copolymer and starch, capable to molding during 45 min and hardening in air under natural conditions, was developed.

(2) It was found that the polymeric composites are biodegradable: they degrade under the action of UV irradiation, micromycetes, and soil microorganisms. The safety of utilization of the material, when buried in the soil, was confirmed.

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