SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

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RESEARCH ARTICLE

Biocomposite materials based on polyethylene and amphiphilic polymer-iron metal complex

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Abstract

Objectives. *To obtain and study the properties including degradability of polymer composite materials (PCM) based on low-density polyethylene (LDPE) obtained by introducing an environmentally friendly additive comprising an oxo-decomposing additive (ODA) based on an amphiphilic polymer-iron metal complex, which accelerates the process of polymer degradation.*

Methods. *PCMs based on LDPE and ODA were produced by processing in laboratory extruders in the form of strands, granules, and films. Thermodynamic properties were determined by differential scanning calorimetry in the temperature range 20–130°C. In order to assess the performance characteristics (physical and mechanical properties) of the PCM, tensile strength and elongation at break were determined. The biodegradability of PCM was evaluated by Sturm's method, with the biodegradation index being determined by the amount of CO_2 gas released as a result of microorganism activity, as well as composting by placing the PCMs for six months in biohumus. Changes in physical and mechanical properties and water absorption of the films during storage were evaluated. The photochemical degradability of the PCM was determined by exposing it to ultraviolet radiation for 100 h (equivalent to approximately one year of exposure of the films under natural conditions). The appearance of the composite samples following removal from the biohumus was determined using an optical microscope with ×50 magnification in transmitted and reflected light.*

Results. *Following biodegradation by composting, the physical and mechanical properties of PCMs decrease by an average of 40.6%. This is related to the structural changes that occur in composites during storage in biohumus, i.e., the formation of a looser structure due to the development of large clusters of microorganisms that affect the formation of microcracks. It leads to the stage of fragmentation of the polyethylene matrix and indicates the progress of biological degradation of composites. In this case, the water absorption of the composite samples was 63% after 96 h of exposure. The biodegradability index determined by the Sturm method after 28 days of bubbling had changed by 82%, indicating an intensive biodegradation process. Exposure to ultraviolet radiation for 96 h resulted in the complete destruction of the PCMs, which turned into small "flakes." This method is the most effective for the degradation of LDPE- and ODA-based PCMs.*

Conclusions. *According to the results of the study of ODA-containing PCMs based on an amphiphilic polymer-iron metal complex, the tested filler-modifier can be recommended for the production of PCMs offering an accelerated degradation period.*

Keywords: *biodegradable compositions, polyethylene, oxo-decomposing additive, amphiphilic polymer-iron metal complex, filler, photochemical destruction*

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НАУЧНАЯ СТАТЬЯ

Биокомпозиционные материалы на основе полиэтилена и амфифильного полимерного металлокомплекса железа

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Аннотация

Цели. *Получение и исследование свойств, а также способности к деструкции полимерных композиционных материалов (ПКМ) на основе полиэтилена низкой плотности (ПЭНП), получаемых за счет введения экологически безопасной оксо-разлагающейся добавки (ОРД) на основе амфифильного полимерного металлокомплекса железа, ускоряющей процесс разложения полимеров.*

Методы. *ПКМ на основе ПЭНП и ОРД получали в лабораторных экструдерах в виде стренг, гранул и пленок. Термодинамические свойства определяли дифференциально-сканирующей калориметрией в интервале температур 20–130 °C. Для оценки эксплуатационных свойств (физико-механических характеристик) ПКМ определяли разрушающее напряжение при растяжении и относительное удлинение при разрыве. Способность к биоразложению ПКМ оценивали методом Штурма, определяя индекс биоразложения по количеству выделившегося CO_2 в результате жизнедеятельности микроорганизмов, а также путем компостирования, помещая ПКМ на полгода в биогумус. В процессе хранения определяли изменение физико-механических свойств, а также водопоглощение пленок. Способность ПКМ к фотохимической деструкции*

определяли, подвергая образцы ультрафиолетовому излучению в отсутствии других источников света в течение 100 ч (эквивалентно приблизительно году экспозиции пленок в природных условиях). Внешний вид композиционных образцов после изъятия из биогумуса определяли при помощи оптического микроскопа с увеличением ×50 в проходящем и отраженном свете.

Результаты. *В процессе биоразложения методом компостирования до полугода физико-механические свойства снижаются, в среднем, на 40.6%, что связано со структурными изменениями, протекающими в композитах в процессе хранения в биогумусе: формированием более рыхлой структуры вследствие образования и продуцирования крупных кластеров микроорганизмов, влияющих на образование микротрещин, что приводит к стадии фрагментации полиэтиленовой матрицы и свидетельствует о протекании процесса биологической деструкции композиционных материалов. При этом водопоглощение композиционных образцов спустя 96 ч экспозиции изменилось на 63%. Индекс биоразлагаемости, определенный методом Штурма по истечении 28 суток барботирования, изменился на 82%, что свидетельствует об интенсивном протекании процесса биоразложения. Воздействие ультрафиолетового излучения в течение 96 ч показало полное разрушение ПКМ до образования мелких «хлопьев». Данный метод является наиболее эффективным для процесса разложения ПКМ на основе ПЭНП и ОРД.*

Выводы. *Исследование ПКМ, содержащих ОРД на основе амфифильного полимерного металлокомплекса железа, показало, что исследуемый наполнитель-модификатор можно рекомендовать для изготовления ПКМ с ускоренным сроком разложения.*

Ключевые слова: *биоразлагаемые композиции, полиэтилен, оксо-разлагающаяся добавка, амфифильный полимерный металлокомплекс железа, наполнитель, фотохимическая деструкция*

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INTRODUCTION

Global production of synthetic plastics increases every year. Polymer materials are used in many areas of light industry, particularly in the packaging industry [1]. Polymeric films used for food packaging, plastic tableware, and rigid polymeric containers are typically used once and then disposed of [2]. Since this type of polymer waste does not decompose over time, its accumulation in landfills or dumps leads to environmental pollution [3]. One of the most environmentally-friendly approaches for eliminating this problem involves the development and use of biodegradable polymer materials based on natural materials that do not harm the environment or human health [4].

To date, a new approach to the production of biodegradable polymeric materials has been developed by producing products that retain their physical and mechanical properties during their service life and subsequently undergo physicochemical, chemical, biological and degradation processes under the influence of environmental factors to be easily incorporated into the metabolism of natural biosystems [5–7].

Biodegradable polymers comprise high-molecular-weight compounds that can be degraded in the presence of active biological organisms and under appropriate conditions. In the active medium, biodegradable polymers undergo significant structural changes in molecular weight and mechanical properties, contributing to the formation

of a nutrient medium for the growth of microorganisms [8–10]. Under such conditions, processes of hydrolysis and photochemical destruction of biodegradable polymers generally occur. Materials break down into components that are part of the natural cycle: water, carbon dioxide, biomass. Unlike traditional polymers derived from petrochemical feedstocks, biodegradable polymers are capable of biodegradation in a short period of time [11–13].

There are several approaches to the development of biodegradable materials, including the use of natural polymers, particularly polysaccharides. In [14, 15], an application for native starch was identified. In [16], native starch was modified into thermoplastic starch to obtain biodegradable hybrid compositions after mixing with polyethylene [17]. The developed composites characterized by optimal physical and mechanical properties had a high biodegradation index [18–20].

Another direction that is gaining popularity in the creation of degradable polymers involves the introduction of molecules into the polymer structure that contain functional groups conducing to accelerated photo- or oxy-decomposition of the polymer [21]. This method seems to be the simplest and relatively cheapest way to solve some environmental problems. It is particularly important that the additives incorporated into the polymer be safe for use in the products made from such a composition [22]. One of the main criteria for biodegradable polymeric materials is the harmlessness of biodegradable materials for the environment and humans, which must be confirmed by international certificates of compliance with international standards adopted in the field of composting and biodegradation (EN 13432 European; ASTM D 6400—USA; and Green PLA—Japanese standards) [23].

Since it is also desirable that the additive be used to modify a range of polymers, an amphiphilic polymer with complexing groups capable of forming stable complexes with metal ions, in particular an amphiphilic polymer-metal complex (APM) of iron, was chosen for the modification of polyethylene in this work. Compared to salts of transition metals (Mn, Co, Cu, Ni, Fe), the toxicity of polymer metal complexes is significantly reduced [24]. Amphiphilic polymers have gained a strong position in many areas of industry, science, technology, and medicine thanks to the successful combination of the physicochemical properties of high molecular compounds and electrolytes [25]. The use of polymer metal complexes as degradation activators incorporated into polymer films is of great importance due to their low toxicity, good compatibility with the hydrophobic matrix of polyolefins, and oxidative activity [26].

MATERIALS AND METHODS

As the objects of the study, we used:

– low-density polyethylene (LDPE) grade 15803-020 produced by *Kazanorgsintez* (Russia), having an average molecular weight of $1.8 \cdot 10^4$ c.u.;

– oxo-decomposing additive (ODA) based on LDPE (50 wt %) and APM (50 wt %) (prooxidants in the form of iron carboxylate);

– polymer composite materials (PCM) based on polyethylene and ODA.

PCMs were obtained on a *Mashplast* extruder (Russia) equipped with either a strand or a flat-plate extrusion head at temperatures in the zones of the extruder ranging from 100°C (in the loading zone) to 125°C (in the head zone).

The melting temperature of the composites was determined by the endothermic maximum of the melting peak using the differential scanning calorimetry (DSC) on a DSC 214 calorimeter (*PolymaNetzsch-Gerätebaug GmbH*, Germany) in the temperature range from 20 to 130°C at a scanning speed of 5 deg/min and a sample weight of 10 ± 1 mg.

The physical and mechanical properties of the samples under tension were determined using the RM-50 testing machine (*Mashplast*, Russia), which is equipped with a computer interface using *StretchTest* software. The destructive tensile stress (σ_p) and elongation at break (ε_p) of the PCM were measured under normal conditions in accordance with GOST 14236-811[1]. The limit of the permissible value of the load measurement error did not exceed ±1%. The maximum deviations in the diameter of the strand samples and the cross-sectional areas of the film samples were ±0.2 mm and 2–3%, respectively. The average value was determined from 3–5 measurements. The tests were carried out at a deformation rate of 100 mm/min. Samples of film for testing were obtained using a special cutting device, the shape of the samples conforming to Type 1B (ENISO 527-3).

A composting method was used to assess the biodegradation dynamics of the PCM. The samples were placed in special trays with biohumus at a temperature of 23 ± 2°C and a humidity of 70 ± 10% and kept for one to six months. The degree of biodegradation of polymer compositions was

[1] GOST 14236-81. USSR State Standard. Polymer films. Tensile test method. Moscow: Izd. Standartov; 1992.

assessed by changes in physical and mechanical properties: destructive tensile stress and elongation at break in accordance with GOST 54530-2011[2].

The Sturm method according to GOST 32433-2013[3] was also used to determine the biodegradation period. This method consists in measuring the assimilation rate of the test material in an aqueous solution in the presence of bacterial microflora, which is recorded by the rate of carbon dioxide emission from the microorganisms. The exposure time was 28 days. To assess biodegradation, the biodegradation rate criterion was used; this is defined as the first derivative of the biodegradability index of PCM.

A determination of the effect of ultraviolet (UV) radiation on the studied PCM was carried out under the following conditions: the films were placed in a chamber isolated from external light sources. Two PRK-4 quartz lamps were used, providing radiation with a wavelength of λ = 185–315 nm. Film samples of 100 × 100 mm were placed at a distance of 30 cm from the UV lamps. 100 h of exposure in such a unit is known to be equivalent to approximately one year of exposure of films under natural conditions.

Optical studies of the appearance of the PCM after composting were carried out using an AxioImagerZ2m microscope (*Carl Zeiss*, Germany) at ×50 magnification in transmitted and reflected light.

RESULTS AND DISCUSSION

LDPE granules were mixed with ODA granules at different concentration ratios, where the share of ODA in film compositions was 1–5% by weight. The mixed extrudate was produced as strands on a twin-screw extruder at the temperatures shown in the table.

The diameter of the extruder screws is 16 mm. The rotation speed of the screws ranged from 60 to 80 rpm. The strands were cut into granules about 2 mm in size at a knife rotation speed from 80 to 100 rpm. The schematic diagram of a twin-screw extruder is shown in Fig. 1.

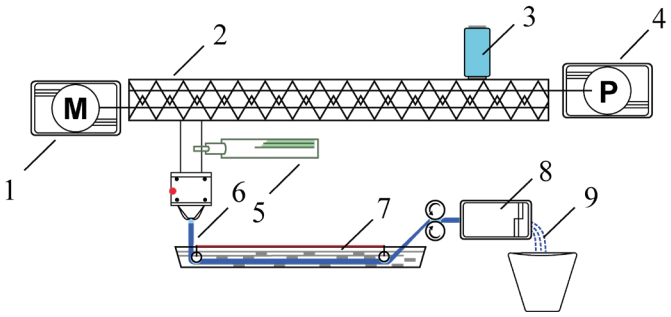


Fig. 1. Scheme of the device for obtaining composite granules: 1 – engine, 2 – twin-screw extruder, 3 – loading hopper, 4 – gearbox synchronized with the engine, 5 – pressure sensor, 6 – strand, 7 – cooling bath, 8 – granulator, and 9 – composite granules.

The pellets obtained on a twin-screw extruder were then fed into a laboratory single-screw extruder with a 12 mm screw diameter and extruded through a 130 mm wide flat die. At the same time, a barrier screw was used, which provided good homogenization of mixtures based on LDPE and ODA during the extrusion process, as well as high quality of the resulting polymer composite

Table. Temperature ranges for composite film fabrication

Composition	Temperature by extruder cylinder zones, °C				
	1 zone	2 zone	3 zone	4 zone	5 zone
LDPE:ODA	100	110	120	125	125

Note: LDPE – low-density polyethylene, ODA – oxo-degradable additive.

[2] GOST 54530-2011. National Standard of the Russian Federation. Resources saving. Packaging. Requirements, criteria and test scheme through composting and biodegradation. Moscow: Standartinform; 2019.

[3] GOST 32433-2013. Interstate Standard. Testing of chemicals of environmental hazard. Ready biodegradability — CO_2 in sealed vessels. Moscow: Standartinform; 2019.

films. The rotation frequency of the screw varied from 60 to 80 rpm.

The material exiting the head was transferred to cooled receiving shafts, then stretched using a broaching device and wound into rolls to produce a composite film material. The diagram of a flat-slot single-screw extruder is shown in Fig. 2. At the same time, the laboratory samples were characterized by a uniform matte surface with no local holes or visible defects. The edges of the samples are even and smooth.

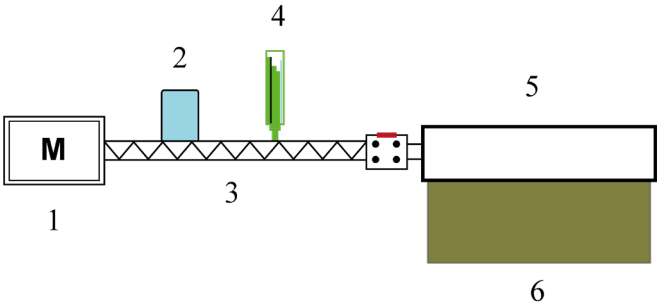


Fig. 2. Scheme of the extrusion device:
1 – engine, 2 – loading hopper, 3 – screw,
4 – pressure sensor, 5 – flat slot head,
and 6 – melt of the finished composite.

The thermodynamic affinity of the components used for the manufacture of PCM was determined using DSC (Fig. 3). The temperature interval at which the technological process of obtaining composites was carried out is selected in the DSC diagram. It can be seen that there are two endo peaks in the diagram, one of which has a weak character and corresponds to the melting temperature of ODA (102.3°C), which can be explained by the low concentration in the composition of the composite. The second peak corresponds to the melting point of the starting polyethylene (111.3°C). Considering that the base of the modifier is comprised of synthetic thermoplastic non-polar polyethylene, this filler is characterized by properties inherent to the original polyolefin due to a narrow range of melting temperatures. This results in a more homogeneous composite structure during the extrusion process.

Water absorption is one of the most important properties of biodegradable compositions, as it indirectly characterizes the ability of the PCM to biodegrade. Figure 4 shows the kinetics of water absorption as a function of ODA concentration in the PCM.

As can be seen, LDPE absorbs virtually no water. For composites where ODA is incorporated at 1–3 wt %, water absorption varies slightly up to 1%.

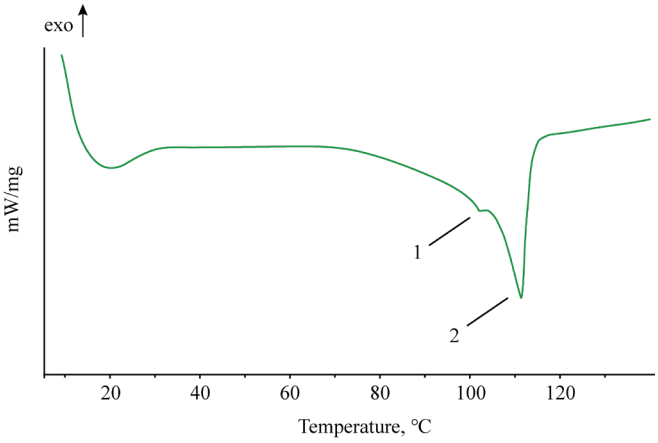


Fig. 3. Differential scanning calorimetry diagram of PCM based on LDPE:ODA = 95:5 wt %.

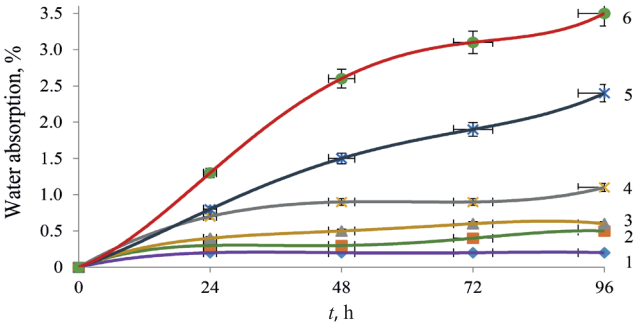


Fig. 4. PCM water absorption kinetics based on LDPE and ODA. 1 – Initial LDPE; ODA content, wt %: 2 – 1; 3 – 2; 4 – 3; 5 – 4; 6 – 5.

A significant change in water absorption was observed for the composite whose ODA mass fraction was 5%. This is probably due to structural changes in the polymer/filler system, where a looser structure is formed in the presence of ODA.

Comprehensive studies of polymer composite film samples to determine biodegradability were carried out using the composting and Sturm method.

The determination of the biodegradation process in biohumus was carried out at a temperature of 23°C and a soil humidity corresponding to 70 ± 10% of its maximum moisture capacity. The used soil was characterized by the presence of microorganisms. The composting times were one month, three months, and six months, respectively. The PCM samples and the control sample were placed on a substrate, pre-filled with a small amount of soil, and then completely covered with a layer of soil; constant

air access to the sample was provided to avoid suppressing the vital activity of the microorganisms. The degree of biodegradation of the samples during storage in biohumus was assessed by changes in parameters of physical and mechanical properties.

The results of determining the destructive tensile stress and elongation at break before and after biodegradation (one month, three months, and six months in biohumus) are shown in Figs. 5 and 6. These figures show that the tensile breaking stress and elongation at break for composites not subjected to biodegradation decrease only slightly and are almost identical to those of the original LDPE, which is characterized by a more homogeneous composite structure.

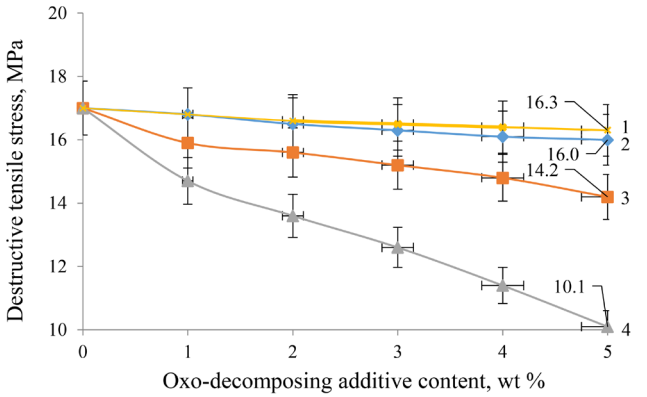


Fig. 5. Determination of tensile destructive stress of PCM based on LDPE and ODA before and after biodegradation: 1 – before biodegradation; 2 – a month of biodegradation; 3 – three months of biodegradation; 4 – six months of biodegradation.

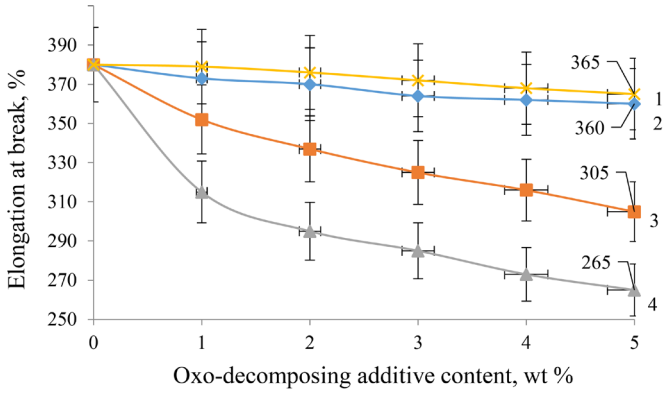
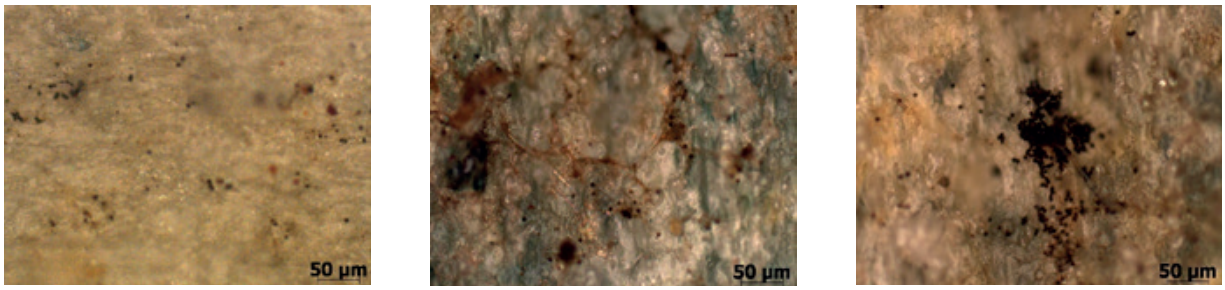


Fig. 6. Elongation at break of PCM based on LDPE and ODA before and after biodegradation: 1 – before biodegradation; 2 – a month of biodegradation; 3 – three months of biodegradation; 4 – six months of biodegradation.

After one month of biodegradation, the values of the destructive tensile stress decrease slightly, most likely due to the formation of microorganism colonies (Fig. 7a). During this period, no structural changes occur in the studied PCM. As the biodegradation period was extended to three months, a 16.5% decrease in mechanical properties was observed. The growth of microbial colonies resulted in a looser structure accompanied by the initial formation of microcracks (Fig. 7b), which characterize the biodegradation of the polyethylene matrix. After six months, the deformation properties had decreased by 25.0% due to active microbial colony growth, while the mechanical properties decreased by 40.6% (Fig. 7c). In addition, not only traces of microorganisms were observed on the composite films studied, but also clusters infected with microcolonies of bacteria. Thus, one group of microorganisms creates a substrate for another, which is characterized by more intensive destruction of composites, contributing to the formation of more microcracks. This indicates the initial stage of fragmentation of the polyethylene matrix and the progression of the biological degradation of composite materials.

The biodegradation index was determined by the Sturm method, which is based on estimating the activity of bacteria by carbon dioxide CO_2 emission. The more CO_2 is released, the higher the rate of biodegradation. During the research, a control flask with biohumus without a laboratory sample was taken as a standard, which excluded the influence of the nutrient medium of the biohumus itself. The rate of biodegradation was taken as the share of increase in CO_2 released as a result of the vital activity of microorganisms in the sample flask compared with the reference. Figure 8 shows the dependence of the determination of the PCM biodegradation index on the concentration of ODA in the PCM.

The observed lack of significant changes occurring during the experiment for LDPE is due to the absence of a structural modifier that contributes to the biological degradation of the polymer. On the other hand, the biodegradability index of the original ODA after 28 days of bubbling is 5.9%; this is due to the absence of a synthetic polymer from which the PCM was obtained. The experimental results for all the LDPE and ODA based composites studied are characterized by almost identical values after one week of bubbling. This is due to the period of initial multiplication of microorganisms, as in the case of biohumus, which were previously in an inactive form. In the period from 7 to 28 days, as the concentration ratio of ODA in composites increases, the biodegradation



(a) (b) (c)

Fig. 7. Photomicrographs of PCM film samples based on LDPE:ODA = 95:5 wt %
after removal from biohumus with an increase of ×50: (a) 1 month; (b) 3 months; (c) 6 months.

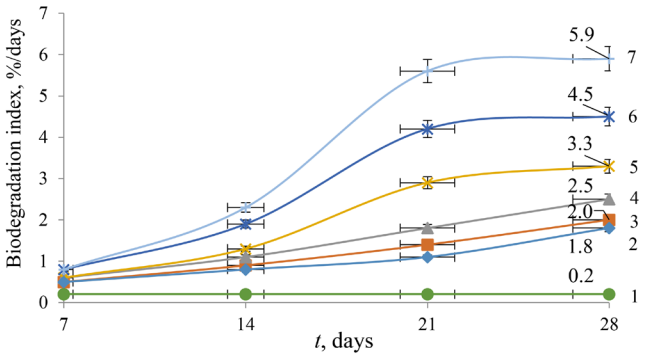


Fig. 8. Dependence of the biodegradation index of PCMs based on LDPE and ODA on ODA content.
1 – Initial LDPE; ODA content, wt %: 2 – 1; 3 – 2; 4 – 3; 5 – 4; 6 – 5; 7 – initial ODA.

index increases, presumably as a result of the active growth of microbial colonies due to the progress of the biodegradation process.

An accelerated test of the effect of UV radiation on the PCM under investigation was carried out. Irradiation of the original LDPE based film for 30 h did not result in any significant change in the properties of the sample: the external characteristics of the film remained the same, while the mechanical properties hardly changed following irradiation. For PCM based on LDPE and ODA with 5% modifier, the decrease in mechanical properties after 30 h of irradiation was 15–30% of the initial value, while no change in appearance was observed (Fig. 9a). The first changes in the appearance of the PCM based on LDPE and ODA at 5 wt % were observed after 60 h of UV exposure. At the same time, the reduction in mechanical properties was 30–55% of the initial value (Fig. 9b). Following 96 h of exposure, the sample was completely destroyed (Fig. 9b).

Thus, the described method turns out to be the most effective for the accelerated process of photochemical destruction of the developed PCMs based on LDPE and ODA based on APM iron.

CONCLUSIONS

Studies were conducted aimed at creating PCMs based on LDPE and ODA from APM iron, having an ODA content in the PCM of 1–5 wt %. Laboratory samples of PCM based on mixtures of LDPE and ODA were obtained by flat-gel extrusion at different concentration ratios.

(a) (b) (c)

Fig. 9. Appearance of PCM based on LDPE:ODA = 95:5 wt % under UV radiation during:
(a) 30 h; (b) 60 h; (c) 96 h.

The physicomechanical properties both before and after the biodegradation process were investigated. Prior to the biodegradation process, optimal physical and mechanical properties of PCM characterized by the thermodynamic compatibility of the components were observed to be practically at the level of LDPE. Following the biodegradation process, a 40.6% decrease in mechanical properties and a 25% decrease in deformation properties due to a change in the structure of the material were observed for a period of up to six months: the formation of a looser structure was accompanied by the formation of colonies of microorganisms with their subsequent reproduction, which in turn influenced the formation of microcracks indicating the initial stage of fragmentation of the polyethylene matrix.

The water absorption of the PCM was determined. It follows from the results of the experiment that the introduction of ODA up to 5 wt % increases the water absorption of the filled compositions by 63%.

The biodegradation of PCM was determined using the Sturm method. The biodegradation process was found to be dependent on the amount of modifier introduced. After 28 days of bubbling, the biodegradation index changed by 82%, indicating that the biodegradation process is progressing.

An accelerated testing process for the resistance of PCM to UV radiation was carried out. Structural changes in the LDPE- and ODA- based PCM were observed to occur at a concentration of 5 wt % ODA start after 60 h of irradiation; these involved a change in the appearance of the sample as well as a decrease in its mechanical properties to 55%. The complete destruction of the sample after 96 h was associated with the formation of small “flakes.”

Based on the obtained data, the use of APM-based ODA of iron as a polyolefin modifier to create biodegradable packaging materials can be recommended.

Acknowledgments

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The author declares no conflicts of interest.

REFERENCES

1. Litvyak V.V. Prospects of manufacture of modern packaging materials with application of biodelessed polymer compositions. *Zhurnal Belorusskogo gosudarstvennogo universiteta. Ekologiya = Journal of the Belarusian State University. Ecology*. 2019;(2):84–94 (in Russ.). URL: https://journals.bsu.by/index.php/ecology/article/view/2711/2295 (Accessed March 30, 2023).

2. Kalia S. *Biodegradable Green Composites*. John Wiley & Sons; 2016. 368 p. ISBN 978-1-11891109-9

3. Skoczinski P., Chinthapalli R., Carus M., Baltus W., de Guzman D., Käb H., Raschka A., Ravenstijn J. *Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2019 – 2024*. Hürth, Germany; 2020. 379 p. URL: https://renewable-carbon.eu/publications/product/bio-based-building-blocks-and-polymers-global-capacities-production-and-trends-2019-2024/ (Accessed March 30, 2023).

СПИСОК ЛИТЕРАТУРЫ

1. Литвяк В.В. Перспективы производства современных упаковочных материалов с применением биоразлагаемых полимерных композиций. *Журнал Белорусского государственного университета. Экология.* 2019;(2):84–94. URL: https://journals.bsu.by/index.php/ecology/article/view/2711/2295 (Дата обращения 30.03.2023).

2. Kalia S. *Biodegradable Green Composites*. John Wiley & Sons; 2016. 368 p. ISBN 978-1-11891109-9

3. Skoczinski P., Chinthapalli R., Carus M., Baltus W., de Guzman D., Käb H., Raschka A., Ravenstijn J. *Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2019 – 2024*. Hürth, Germany; 2020. 379 p. URL: https://renewable-carbon.eu/publications/product/bio-based-building-blocks-and-polymers-global-capacities-production-and-trends-2019-2024/ (Дата обращения 30.03.2023).

4. Nishat N., Malik A. Synthesis, spectral characterization thermal stability, antimicrobial studies and biodegradation of starch–thiourea based biodegradable polymeric ligand and its coordination complexes with [Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)] metals. *J. Saudi Chem. Soc*. 2016;20(Suppl. 1):S7–S15. https://doi.org/10.1016/j.jscs.2012.07.017

5. Sudhakar Y.N., Selvakumar M. Lithium perchlorate doped plasticized chitosan and starch blend as biodegradable polymer electrolyte for supercapacitors. *Electrochimica Acta*. 2012;78:398–405. https://doi.org/10.1016/j.electacta.2012.06.032

6. Mendes J.F., Paschoalin R.T., Carmona V.B., Sena Neto A.R., Marques A.C.P., Marconcini J.M., Mattoso L.H.C., Medeiros E.S., Oliveira J.E. Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion. *Carbohydr. Polym*. 2016;137:452–458. https://doi.org/10.1016/j.carbpol.2015.10.093

7. Nguyen D.M., Do T.V.V., Grillet A.-C., Thuc H.H., Thuc C.N.H. Biodegradability of polymer film based on low density polyethylene and cassava starch. *Int. Biodeterior. Biodegradation*. 2016;115:257–265. https://doi.org/10.1016/j.ibiod.2016.09.004

8. Tang X., Alavi S. Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability. *Carbohydr. Polym*. 2011;85(1):7–16. https://doi.org/10.1016/j.carbpol.2011.01.030

9. Singh R., Sharma R., Shaqib M., Sarkar A., Dutt Chauhan K. Biodegradable polymers as packaging materials. In: *Biopolymers and their Industrial Applications. From Plant, Animal, and Marine Sources, to Functional Products*. 2021. Chapter 10. P. 245–259. https://doi.org/10.1016/B978-0-12-819240-5.00010-9

10. Ojogbo E., Ogunsona E.O., Mekonnen T.H. Chemical and physical modifications of starch for renewable polymeric materials. *Materials Today Sustainability*. 2020;7–8:100028. https://doi.org/10.1016/j.mtsust.2019.100028

11. Tudorachi N., Cascaval C.N., Rusu M., Pruteanu M. Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials. *Polym. Test*. 2000;19(7):785–799. https://doi.org/10.1016/S0142-9418(99)00049-5

12. Fonseca-García A., Jiménez-Regalado E., Aguirre-Loredo R.Y. Preparation of a novel biodegradable packaging film based on corn starch-chitosan and poloxamers. *Carbohydr. Polym*. 2021;251:117009. https://doi.org/10.1016/j.carbpol.2020.117009

13. Mittal A., Garg S., Bajpai S. Fabrication and characteristics of poly (vinyl alcohol)-starch-cellulosic material based biodegradable composite film for packaging application. *Materials Today: Proceedings*. 2020;21(3):1577–1582. https://doi.org/10.1016/j.matpr.2019.11.210

14. Vasilyev I.Yu., Ananyev V.V., Kolpakova V.V., Sardzhveladze A.S. Development of technology for producing biodegradable hybrid composites based on polyethylene, starch, and monoglycerides. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2020;15(6):44–55 (in Russ.). https://doi.org/10.32362/2410-6593-2020-15-6-44-55

15. Papakhin AA, Kolpakova V.V., Borodina Z.M., Sardzhveladze A.S., Vasilyev I.Yu. Modified porous starch in development of biodegradable composite polymer materials. *Tekhnika i tekhnologiya pishchevykh proizvodstv = Food Processing: Techniques and Technology*. 2020;50(3):549–558 (in Russ.). https://doi.org/10.21603/2074-9414-2020-3-549-558

4. Nishat N., Malik A. Synthesis, spectral characterization thermal stability, antimicrobial studies and biodegradation of starch–thiourea based biodegradable polymeric ligand and its coordination complexes with [Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)] metals. *J. Saudi Chem. Soc*. 2016;20(Suppl. 1):S7–S15. https://doi.org/10.1016/j.jscs.2012.07.017

5. Sudhakar Y.N., Selvakumar M. Lithium perchlorate doped plasticized chitosan and starch blend as biodegradable polymer electrolyte for supercapacitors. *Electrochimica Acta*. 2012;78:398–405. https://doi.org/10.1016/j.electacta.2012.06.032

6. Mendes J.F., Paschoalin R.T., Carmona V.B., Sena Neto A.R., Marques A.C.P., Marconcini J.M., Mattoso L.H.C., Medeiros E.S., Oliveira J.E. Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion. *Carbohydr. Polym*. 2016;137:452–458. https://doi.org/10.1016/j.carbpol.2015.10.093

7. Nguyen D.M., Do T.V.V., Grillet A.-C., Thuc H.H., Thuc C.N.H. Biodegradability of polymer film based on low density polyethylene and cassava starch. *Int. Biodeterior. Biodegradation*. 2016;115:257–265. https://doi.org/10.1016/j.ibiod.2016.09.004

8. Tang X., Alavi S. Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability. *Carbohydr. Polym*. 2011;85(1):7–16. https://doi.org/10.1016/j.carbpol.2011.01.030

9. Singh R., Sharma R., Shaqib M., Sarkar A., Dutt Chauhan K. Biodegradable polymers as packaging materials. In: *Biopolymers and their Industrial Applications. From Plant, Animal, and Marine Sources, to Functional Products*. 2021. Chapter 10. P. 245–259. https://doi.org/10.1016/B978-0-12-819240-5.00010-9

10. Ojogbo E., Ogunsona E.O., Mekonnen T.H. Chemical and physical modifications of starch for renewable polymeric materials. *Materials Today Sustainability*. 2020;7–8:100028. https://doi.org/10.1016/j.mtsust.2019.100028

11. Tudorachi N., Cascaval C.N., Rusu M., Pruteanu M. Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials. *Polym. Test*. 2000;19(7):785–799. https://doi.org/10.1016/S0142-9418(99)00049-5

12. Fonseca-García A., Jiménez-Regalado E., Aguirre-Loredo R.Y. Preparation of a novel biodegradable packaging film based on corn starch-chitosan and poloxamers. *Carbohydr. Polym*. 2021;251:117009. https://doi.org/10.1016/j.carbpol.2020.117009

13. Mittal A., Garg S., Bajpai S. Fabrication and characteristics of poly (vinyl alcohol)-starch-cellulosic material based biodegradable composite film for packaging application. *Materials Today: Proceedings*. 2020;21(3):1577–1582. https://doi.org/10.1016/j.matpr.2019.11.210

14. Васильев И.Ю., Ананьев В.В., Колпакова В.В., Сарджвеладзе А.С. Разработка технологии получения биоразлагаемых композиций на основе полиэтилена, крахмала и моноглицеридов. *Тонкие химические технологии.* 2020;15(6):44–55. https://doi.org/10.32362/2410-6593-2020-15-6-44-55

15. Папахин А.А., Колпакова В.В., Бородина З.М., Сарджвеладзе А.С., Васильев И.Ю. Применение модифицированного пористого крахмала для создания биоразлагаемых композиционных полимерных материалов. *Техника и технология пищевых производств*. 2020;50(3):549–558. http://doi.org/10.21603/2074-9414-2020-3-549-558

16. Vasilyev I.Yu., Ananyev V.V., Chernov M.E. Biodegradable packaging materials based on low density polyethylene, starch and monoglycerides. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2022;17(3):231–241 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2022-17-3-231-241

17. Vasiliev I.Yu., Ananyev V.V., Kolpakova V.V., Sardzhveladze A.S. Biodegradable materials based on low-density polyethylene, starch and monoglycerides. *Vse Materialy. Entsiklopedicheskii Spravochnik = All Materials. Encyclopedic Reference Manual*. 2021;(11):20–26 (in Russ.). https://doi.org/10.31044/1994-6260-2021-0-11-20-26

18. Vasilyev I., Ananiev V., Sultanova Yu., Kolpakova V. Effect of the biodegradable compounds composition with monoglycerides on mechanical properties. In: *Materials Science Forum*. 2021;1031:7–16. https://doi.org/10.4028/www.scientific.net/MSF.1031.7

19. Vasil'ev I.Y., Anan'ev V.V., Sultanova Y.M., Kolpakova V.V. The influence of the composition of polyethylene, starch, and monoglyceride biodegradable compositions on their physicomechanical properties and structure. *Polym. Sci. Ser. D.* 2022;15(1):122–127. https://doi.org/10.1134/S1995421222010257

20. Lukin N.D., Kolpakova V.V., Usachev I.S., Sardzhvelazhdze A.S., Solomin D.A., Vasil'ev I.Yu. Modification of polymer compositions with thermoplastic starch for bio-dependable packaging products. In: *Biotekhnologiya: sostoyanie i perspektivy razvitiya: Materialy mezhdunarodnogo kongressa* (*Biotechnology: State of the Art and Perspectives: Proceedings of the International Congress*). Moscow: RED GROUP; 2019. P. 102–104 (in Russ.).

21. Tabasum S., Younas M., Zaeem M.A., Majeed I., Majeed M., Noreen A., Iqbal N.M., Zia K.M. A review on blending of corn starch with natural and synthetic polymers, and inorganic nanoparticles with mathematical modeling. *Int. J. Biol. Macromol*. 2019;122:969–996. https://doi.org/10.1016/j.ijbiomac.2018.10.092

22. Ren H., Ouyang G., Iyer S.S., Yang Y.-T. Mechanism and process window study for die-to-wafer (D_2W) hybrid bonding. *ECS J. Solid State Sci. Technol.* 2021;10(6):064008. https://doi.org/10.1149/2162-8777/ac0a52

23. Tokareva N.E. Evaluation of the rate of decomposition of polyethylene with D_2W additive. In: *Innovatsionnye faktory razvitiya transporta. Teoriya i praktika. Materialy mezhdunarodnoi nauchno-prakticheskoi konferentsii* (*Innovative Factors of Transport Development. Theory and Practice. Materials of the International Scientific and Practical Conference*). Novosibirsk: STU; 2018. P. 79–81 (in Russ.).

24. Obydenova A.A., Myalenko D.M. Study of physical, mechanical and organoleptic characteristics of biodegradable polymer packaging based on polyethylene modified with oxo-additive D_2W. In: *Sbornik tezisov X Mezhdunarodnoi nauchnoi konferentsii studentov, aspirantov i molodykh uchenykh* (*Food Innovation and Biotechnology. Collection of Abstracts of the 10th International Scientific Conference of Students, Graduate Students and Young Scientists*). V. 1. Kemerovo: KemSU; 2022. P. 298–300 (in Russ.).

25. Ershova O.V., Bodyan L.A., Ponomarev A.P., Bakhaeva A.N. The effect of chemical destruction on the change in physical and mechanical properties of polymer films with D_2W additive. *Sovremennye problemy nauki i obrazovaniya = Modern Problems of Science and Education.* 2015;1(1):1981 (in Russ.).

26. Lukanina Yu.K., Khvatov A.V., Koroleva A.V., Popov A.A., Kolesnikova N.N. *Okso-razlagayushchaya dobavka k poliolefinam* (*Oxo-decomposing additive for polyolefins*): RF Pat. 2540273 C1. Publ. 10.02.2015 (in Russ.).

16. Васильев И.Ю., Ананьев В.В., Чернов М.Е. Биоразлагаемые упаковочные материалы на основе полиэтилена низкой плотности, крахмала и моноглицеридов. *Тонкие химические технологии.* 2022;17(3):231–241. https://doi.org/10.32362/2410-6593-2022-17-3-231-241

17. Васильев И.Ю., Ананьев В.В., Колпакова В.В, Сарджвеладзе А.С. Биоразлагаемые материалы на основе ПЭНП, крахмала и моноглицеридов. *Все материалы. Энциклопедический справочник.* 2021;(11):20–26. https://doi.org/10.31044/1994-6260-2021-0-11-20-26

18. Vasilyev I., Ananiev V., Sultanova Yu., Kolpakova V. Effect of the biodegradable compounds composition with monoglycerides on mechanical properties. In: *Materials Science Forum*. 2021;1031:7–16. https://doi.org/10.4028/www.scientific.net/MSF.1031.7

19. Vasil'ev I.Y., Anan'ev V.V., Sultanova Y.M., Kolpakova V.V. The influence of the composition of polyethylene, starch, and monoglyceride biodegradable compositions on their physicomechanical properties and structure. *Polym. Sci. Ser. D.* 2022;15(1):122–127. https://doi.org/10.1134/S1995421222010257

20. Лукин Н.Д., Колпакова В.В., Усачев И.С., Сарджвеладзе А.С., Соломин Д.А., Васильев И.Ю. Модификация полимерных композиций с термопластичным крахмалом для биоразлагаемой упаковочной пленки. В сб.: *Биотехнология: состояние и перспективы развития: Материалы международного конгресса*. М.: ООО «РЭД ГРУПП»; 2019. С. 102–104.

21. Tabasum S., Younas M., Zaeem M.A., Majeed I., Majeed M., Noreen A., Iqbal N.M., Zia K.M. A review on blending of corn starch with natural and synthetic polymers, and inorganic nanoparticles with mathematical modeling. *Int. J. Biol. Macromol*. 2019;122:969–996. https://doi.org/10.1016/j.ijbiomac.2018.10.092

22. Ren H., Ouyang G., Iyer S.S., Yang Y.-T. Mechanism and process window study for die-to-wafer (D2W) hybrid bonding. *ECS J. Solid State Sci. Technol.* 2021;10(6):064008. https://doi.org/10.1149/2162-8777/ac0a52

23. Токарева Н.Е. Оценка скорости разложения полиэтилена с добавкой D2W. В сб.: *Инновационные факторы развития транспорта. Теория и практика. Материалы международной научно-практической конференции.* Новосибирск: СГУПС; 2018. С. 79–81.

24. Обыденова А.А., Мяленко Д.М. Исследование физико-механических и органолептических характеристики биоразлагаемой полимерной упаковки на основе полиэтилена, модифицированного оксо-добавкой D2W. В сб.: *Пищевые инновации и биотехнологии. Сборник тезисов X Международной научной конференции студентов, аспирантов и молодых ученых*. Т. 1. Кемерово: КемГУ; 2022. С. 298–300.

25. Ершова О.В., Бодьян Л.А., Пономарев А.П., Бахаева А.Н. Влияние химической деструкции на изменение физико-механических свойств упаковочных полимерных пленок с добавкой D2W. *Современные проблемы науки и образования*. 2015;1(1):1981.

26. Луканина Ю.К., Хватов А.В., Королева А.В., Попов А.А., Колесникова Н.Н. *Оксо-разлагающая добавка к полиолефинам*: Пат. 2540273 C1 РФ. Заявка № 2013155023/04; заявл. 12.12.2013; опубл. 10.02.2015.

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