SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

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RESEARCH ARTICLE

Biodegradable packaging materials based on low density polyethylene, starch and monoglycerides

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Abstract

Objectives. *To investigate the production and biological degradation of biodegradable hybrid compositions (BHCs), dispersed-filled with starch-containing products of various origins and distilled monoglycerides, along with the biodegradation of compositions based on low density polyethylene and thermoplastic starch (TPS) of various origins: corn, pea, and rice.*
Methods. *Thermoplastic starch was obtained based on native starches of several types, which were processed in Brabender and MashkPlast (Russia) laboratory extruders. BHCs in the form of strands, granules, and films were obtained by mixing thermoplastic starches with polyethylene in extruders. Structural BHC parameters were studied by optical and electron scanning microscopy. The biodegradability of the composite films was evaluated by placing them in biohumus for six months; during storage, the change in water absorption of the films was determined. Before and after the biodegradation process, tensile fracture stress and elongation at rupture were determined to evaluate BHC performance (physical and mechanical characteristics of films). Changes in the chemical structure during biodegradation were determined by Fourier infrared spectroscopy.*

Results. *The positive effect (acceleration of the biodegradation process) of using a novel type of starch plasticizer—monoglycerides distilled in TPS–polyethylene compositions—was confirmed. After six months, intensive sporulation of active microorganisms was observed on the surface of the samples. At the same time, water absorption by the samples reached 30%. The observed 60% decrease in strength and deformation properties indicates an intensive process of biodegradation.*
Conclusions. *The biodegradation rate was shown to depend on the concentration and even distribution of the natural biodegradable filler in the synthetic polymer composition.*

Keywords: *biodegradable compositions, polyolefins, thermoplastic starch, modifier, filler, biodegradation*

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НАУЧНАЯ СТАТЬЯ

Биоразлагаемые упаковочные материалы на основе полиэтилена низкой плотности, крахмала и моноглицеридов

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Аннотация

Цели. *Исследовать процесс производства биоразрушаемых гибридных композиций (БГК), дисперсно-наполненных крахмалсодержащими продуктами различного происхождения и дистиллированными моноглицеридами, и их биологическую деструкцию, а также процесс биоразложения композиций на основе полиэтилена низкой плотности и термопластичного крахмала (ТПК) различного происхождения: кукурузного, горохового и рисового.*
Методы. *Термопластичный крахмал получали на основе нативных крахмалов разных видов путем переработки их в лабораторных экструдерах фирм «Брабендер» и «МашПласт» (Россия). Смешивая в экструдерах термопластичные крахмалы с полиэтиленом, получали БГК в виде стренг, гранул и пленок. Структурные параметры БГК изучали методами оптической и электронной сканирующей микроскопии. Способность к биоразложению композитных пленок оценивали, помещая их на полгода в биогумус, и в процессе хранения определяли изменение водопоглощения пленок. Для оценки эксплуатационных свойств (физико-механических характеристик пленок) БГК определяли разрушающее напряжение при растяжении и относительное удлинение при разрыве до и после процесса биоразложения. Изменения химической структуры в процессе биоразложения определяли методом инфракрасной спектроскопии с преобразованием Фурье.*
Результаты. *Подтвержден положительный эффект (ускорение процесса биоразложения) от использования нового типа пластификатора крахмала – дистиллированных моноглицеридов в композициях ТПК–полиэтилен. По истечении полугода на поверхности*

образцов наблюдали интенсивное сороношение активных микроорганизмов. При этом водопоглощение образцов достигало 30%, прочностные и деформационные свойства снизились на 60%, что свидетельствует об интенсивном протекании процесса биоразложения.

Выводы. *Установлено, что скорость процесса биоразложения композиций зависит от концентрационного соотношения вводимого ТПК, а также от его равномерного распределения в синтетическим полимере.*

Ключевые слова: *биоразлагаемые композиции, полиолефины, термопластичный крахмал, моноглицериды, наполнитель, деструкция*

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INTRODUCTION

The global production of synthetic plastics is increasing every year. Polymeric materials are used in many branches of light industry and, especially, in the packaging industry [1]. In most cases, polymer films used for food packaging, plastic utensils, and rigid polymer containers are used once and then discarded [2]. Such “polymer waste” does not decompose for a long time, but instead accumulates in landfills or disposal sites to pollute the environment[1] [3]. In order to mitigate this problem, one of the most acceptable and already applied approaches involves the creation and use of biodegradable polymeric materials based on natural materials that do not harm the environment or human health [4].

A novel approach developed for the manufacture of biodegradable polymeric materials envisages the manufacture of products that retain their physical and mechanical characteristics only for the period of intended use. Afterwards, they are subjected to various destructive normal physicochemical, chemical, and biological processes under the influence of environmental factors to re-enter the metabolism of natural biosystems [5, 6].

Biodegradable polymers are macromolecular compounds capable of being degraded in the presence of active biological organisms in appropriate conditions. In an active medium, biodegradable polymers undergo significant changes in molecular weight and mechanical characteristics, themselves contributing to the formation of a nutrient medium for the growth of microorganisms [7–9]. In such media, hydrolysis and photochemical destruction of biodegradable polymers typically take place. Materials break down into components involved in the natural cycle: water, carbon dioxide, and biomass. In contrast to traditional polymers obtained from petrochemical raw materials, biodegradable polymers are characterized by their ability to decompose into components of biological life within a short period of time [10–12].

While a variety of natural polymers are used in the manufacture of biodegradable compositions, starch is one of the most important. This polysaccharide, which is present in many types of plants in the form of tubers, seeds, stems, and leaves, is typically produced from potato, rice, pea, wheat, or corn feedstocks [13, 14].

Conventionally, the processes for obtaining biodegradable polymeric materials can be divided into:

1) mixing native starch with synthetic polymers (polyethylene, polypropylene, etc.);

2) mixing native starch with natural polymers;

3) obtaining thermoplastic starch (TPS) [15–17].

In order to solve the problem of recycling packaging materials, one of the most promising directions involves the creation of biocomposites that combine the useful properties of TPS and synthetic polymers [18].

[1] Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2019–2024. Hüerth, Germany; 2020. URL: http://bio-based.eu/downloads/bio-based-building-blocks-and-polymers-global-capacities-production-and-trends-2019-2024/

When manufacturing TPS, selection of the appropriate type of plasticizer is of great importance for ensuring the desired mechanical properties. In addition to starch and glycerin, sorbitol has long been used in the production of TPS. However, as follows from the results of studies [19–21], the use of sorbitol as a plasticizer for the manufacture of TPS subsequently used as a biodegradable hybrid composition (BHC) component is not suitable for all types of native starches.

The authors of the article [22] found a substitute for sorbitol. As plasticizers, they used monoesters of glycerol and higher fatty acids—distilled monoglycerides (DMG), [$CH_2OH–(CHOH)_4–CH_2–OCO–R$] [23]. As well as having higher physical and mechanical properties, biocomposite polymer films based on DMG also have a higher biodegradation index.

MATERIALS AND METHODS

Materials

The study used:

– low-density polyethylene (LDPE), 11503-070 brand (*Kazanorgsintez*, Russia), with an average molecular weight of 1.8·104 Da;

– glycerin, PK-94 grade, density 1240 kg/m^3 (*Vympel*, Russia), GOST 6824-96[2];

– distilled DMG produced according to TU 10-1197-95[3] specifications (*RusKhimtrade*, Russia);

– corn starch (*Krakhmalprodukt*, Russia), GOST 32159-2013[4];

– rice starch (*Vinh Thuan Trading Import-Export*, Vietnam);

– pea starch (*Roquette*, France);

– composite starch-containing materials based on polyethylene (PE) and TPS.

Research methods

BHC samples were obtained in an extruder (*MashPlast*, Russia) equipped with either a strand or a flat-slot extrusion head, at temperatures in the extruder zones from 115 (in the loading zone) to 140°C (in the head zone) [24].

The physical and mechanical properties of the samples under tension were determined using a testing machine RM-50 (*MashPlast*, Russia) equipped with a computer interface running the StretchTest software. The tensile stress at break (σ_b) and relative elongation at break (ε_b) of BHC were measured under normal conditions according to GOST 14236-81[5]. The limit of the permissible value of the load measurement error did not exceed ±1%. The limiting deviations in the diameter of strand samples and the cross-sectional areas of film samples were ±0.2 mm and 2–3%, respectively. The mean value was determined after 3–5 measurements. The tests were carried out at a strain rate of 100 mm/min. Film samples for testing were obtained using a special punching device. The samples shape was of type 1B (EN ISO 527-3[6]).

The water absorption of the studied BHC was determined according to GOST 4650-80[7].

In order to assess BHC biodegradation dynamics, the composting method was used. The samples were placed in special trays with biohumus at a temperature of 23 ± 2°C and a humidity of 70 ± 10% and kept from one month to six months. The degree of biodegradation of the polymer compositions was assessed in terms of changes in their physical and mechanical properties: breaking tensile stress (σ_t) and relative elongation at break (ε_b), according to GOST 54530-2011[8].

Optical studies of BHC appearance after composting were carried out using an Axio Imager.Z2m microscope (*Carl Zeiss*, Germany) in transmitted and reflected light at ×50 and ×200 magnifications.

The chemical structure of BHC was studied by Fourier-transform infrared spectroscopy (FTIR) on an FSM-1201 device (*EuroLab*, Russia) equipped by a multiple frustrated total internal reflection attachment with a resolution of 1.0 cm^{-1} (spectral range of wavenumbers 375–7900 cm^{-1}).

RESULTS AND DISCUSSION

When creating biodegradable composite polymer materials, it is necessary to take into account their technological, operational, and other properties, as well as data characterizing the rate of their biodegradation. One of the most important requirements for a created composite material is the preservation of the

[2] GOST 6824-96. Interstate Standard. Distilled glycerine. General specifications. Moscow: Izd. Standartov; 1997.

[3] TU 10-1197-95. Distilled monoglycerides. Technical conditions.

[4] GOST 32159-2013. Interstate Standard. Maize starch. General specifications. Moscow: Standartinform; 2019.

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

[6] ISO 527-3. International Standard. Plastics — Determination of tensile properties. Part 3: Test conditions for films and sheets. Second edition, 2018-11. URL: https://cdn.standards.iteh.ai/samples/70307/e804daa78e2747a6bbd08ac486d58225/ISO-527-3-2018.pdf

[7] GOST 4650-80. Interstate Standard. Plastics. Methods for the determination of water absorption. Moscow: Izd. Standartov; 2008.

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

technological characteristics inherent in the main polymer in order to ensure the possibility of its processing on standard equipment [25].

At the first stage of the work, BHC was prepared based on LDPE and TPS of various origins: corn, pea, and rice. The required range of concentration ratios of the components was chosen, in which the share of TPS is from 40 to 60 wt %, respectively [22].

The next stage of the study involved establishing the terms of biodegradation of the obtained compositions. To do this, a combination of several methods was used: composting in biohumus and assessing water absorption. Water is a necessary component for the vital activity of microorganisms. In addition, when water penetrates into the surface layers and diffuses deep into the material structure, it can have a plasticizing effect.

The results of the water absorption study are presented in Table 1. It can be seen that LDPE practically does not absorb water, while compositions modified with starch absorb it in significant amounts; moreover, as the TPS content in the compositions increases, water absorption also increases. It can be assumed that this is due to the structural processes occurring in the polymer–filler system. As the polymer matrix is loosened, the free volume between the macromolecules increases. This leads to an increase in the amount of absorbed water. The composition based on rice TPS has the highest water absorption among the studied BHS. It is logical to assume that this composition will be more rapidly biodegradable when it enters the soil.

The course of the biodegradation process was judged by the results of optical microscopy, as well as by observed changes in the physicochemical properties of the studied materials following their exposure in the soil.

The experiment was carried out at a temperature of 23°C and a soil moisture content corresponding to 70 ± 10% of its maximum moisture capacity. Composting times were one, three, and six months. BHC samples and a control PE sample were placed on a soil substrate and completely covered with a layer of soil, while providing constant air access to

Table 1. Results of BHC water absorption

Composition, wt %	Water absorption, %
Raw LDPE	0.2
BHC (TPS:PE corn starch 60:40)	7.6
BHC (TPS:PE corn starch 50:50)	4.1
BHC (TPS:PE corn starch 40:60)	2.3
BHC (TPS:PE pea starch 60:40)	7.9
BHC (TPS:PE pea starch 50:50)	3.8
BHC (TPS:PE pea starch 40:60)	2.1
BHC (TPS:PE rice starch 60:40)	8.1
BHC (TPS:PE rice starch 50:50)	5.6
BHC (TPS:PE rice starch 40:60)	2.5

Note: LDPE is low density polyethylene, BHCs are biodegradable hybrid compositions, TPS is thermoplastic starch, and PE is polyethylene.

the sample in order to avoid suppression of the vital activity of the microorganisms.

Figure 1 shows microphotographs of BHC samples of composition TPS:LDPE = 60:40 after six months of keeping in biohumus.

As can be seen from the presented microphotographs, local development of soil microorganisms occurs on the surface of the composite samples. While the amount of TPS introduced has little effect on the process during the initial period, the dynamics of microbial growth on different samples at the same content of TPS of different origin is not the same. The sample based on corn TPS (1) is characterized by surface development of microorganisms without intensive sporulation, while the samples based on pea TPS (2) and rice TPS (3) clearly show continuous growth of microorganisms, as well as intensive sporulation. The compositions have a loose structure and surface defects, and the destruction of the filler is observed throughout the entire volume of the samples.

The results of determining the tensile stress at break (σ_b) and relative elongation at break (ε_b) for BHC after half a year of composting are presented in Table 2.

As follows from the obtained data, following a six-month period of keeping the samples in biohumus with soil microorganisms, their physical and

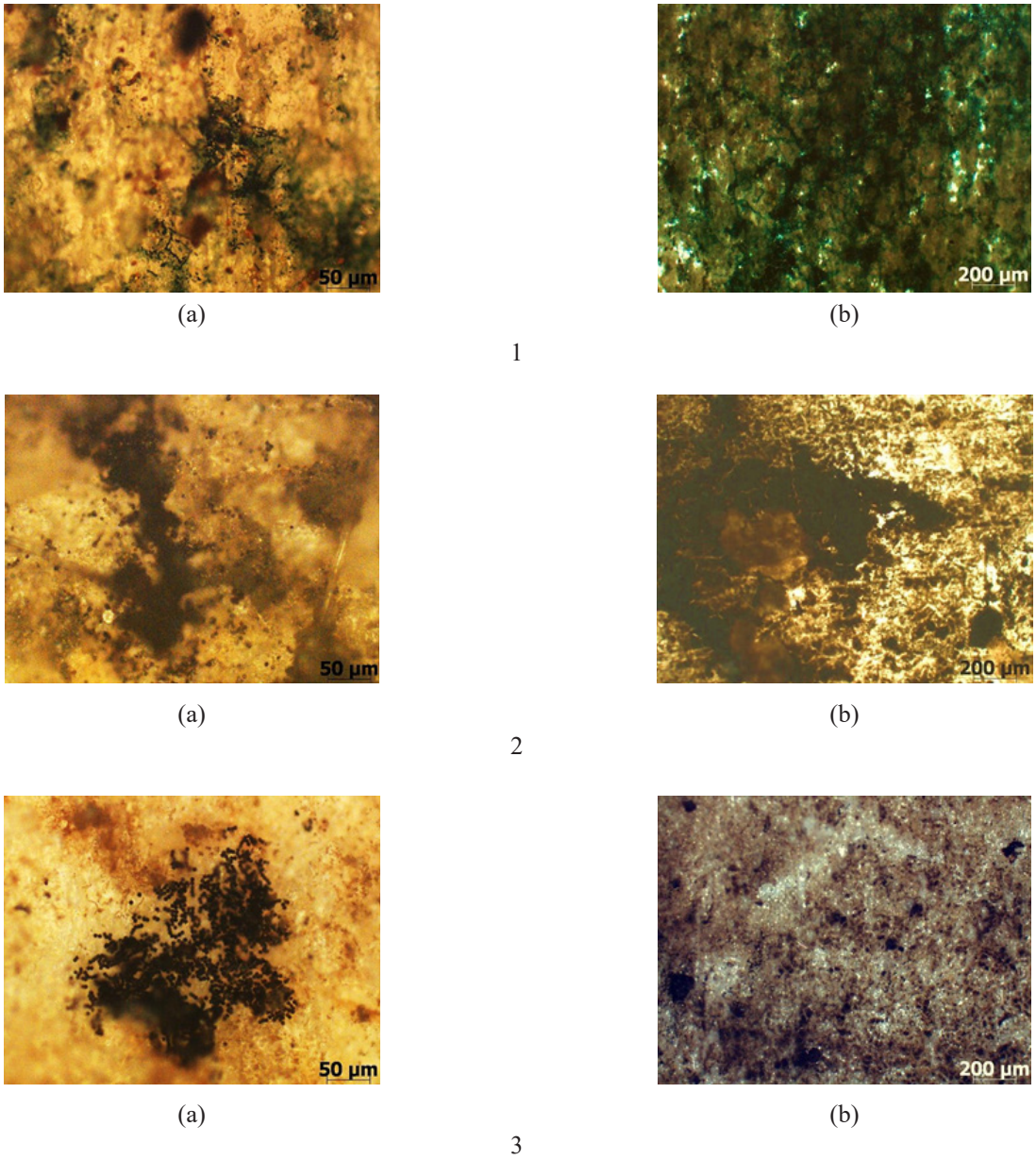

Fig. 1. Micrographs of film samples after removal from biohumus
(1) corn starch BHC, (2) pea starch BHC, (3) rice starch BHC
(a) increase ×50, (b) increase ×200.

mechanical characteristics deteriorate. In the process of biodegradation, water is absorbed by composite samples, resulting in a change in the material structure. It is likely that the intermolecular interactions that hold the polymer matrix and filler weaken together to produce visible defects: the formation of a loose surface structure due to the filler destruction over the entire surface of the samples. In the case of BHC based on corn starch, a 1.5-fold deterioration in physical and mechanical properties occurs; in BHC based on pea starch—a 1.3-fold change; in BHC based on rice starch—a 2.1-fold change. This supports the conclusion that the studied film compositions will biodegrade quickly under conditions of disposal.

In order to further assess the changes that occurred during biodegradation, spectral characteristics were determined using the FTIR method. As an example, Fig. 2 shows the spectrum of BHC based on rice TPS at a ratio of TPS:LDPE = 60:40 wt % before and after the biodegradation process.

First of all, it is of interest to estimate the intensity of the OH groups absorption bands located between 3000 and 3600 cm^{-1}, as well as that of the bands between 1000–1500 cm^{-1}, which are characteristic of CH_2, CH_3, and C–O groups. While the middle and far regions of the IR spectrum are less informative, they support the conclusion that the BHC–PE composition contains functional groups characteristic of fatty acids (forming part of DMG) in OH-groups of glycerol, as well as functional groups of starch.

Following six months of keeping BHC in biohumus, absorption peaks appear in the IR spectrum in the region of 1000–1200 cm^{-1}, indicating the

Table 2. Results of physical and mechanical tests of BHC before and after biodegradation process

TPS:PE ratio	σ_b, MPa (Δ ± 0.2)	ε_b, % (Δ ± 5)	σ_b, MPa (Δ ± 0.2)	ε_b, % (Δ ± 5)
1. 100% PE	16	195	–	–
–	With DMG before biodegradation		With DMG after biodegradation	
2. TPS based on corn				
60:40	10.9	78	7.2	45
50:50	11.6	84	8.3	67
40:60	12.8	93	10.3	84
3. TPS based on peas				
60:40	7.8	82	5.6	48
50:50	9.3	91	8.4	64
40:60	10.1	102	9.3	86
4. TPS based on rice				
60:40	11.2	96	5.2	41
50:50	11.9	104	7.3	56
40:60	12.8	115	8.9	87

Note: σ_b is a tensile stress at break, ε_b is a relative elongation at break, DMGs are distilled monoglycerides, TPS is thermoplastic starch, and PE is polyethylene.

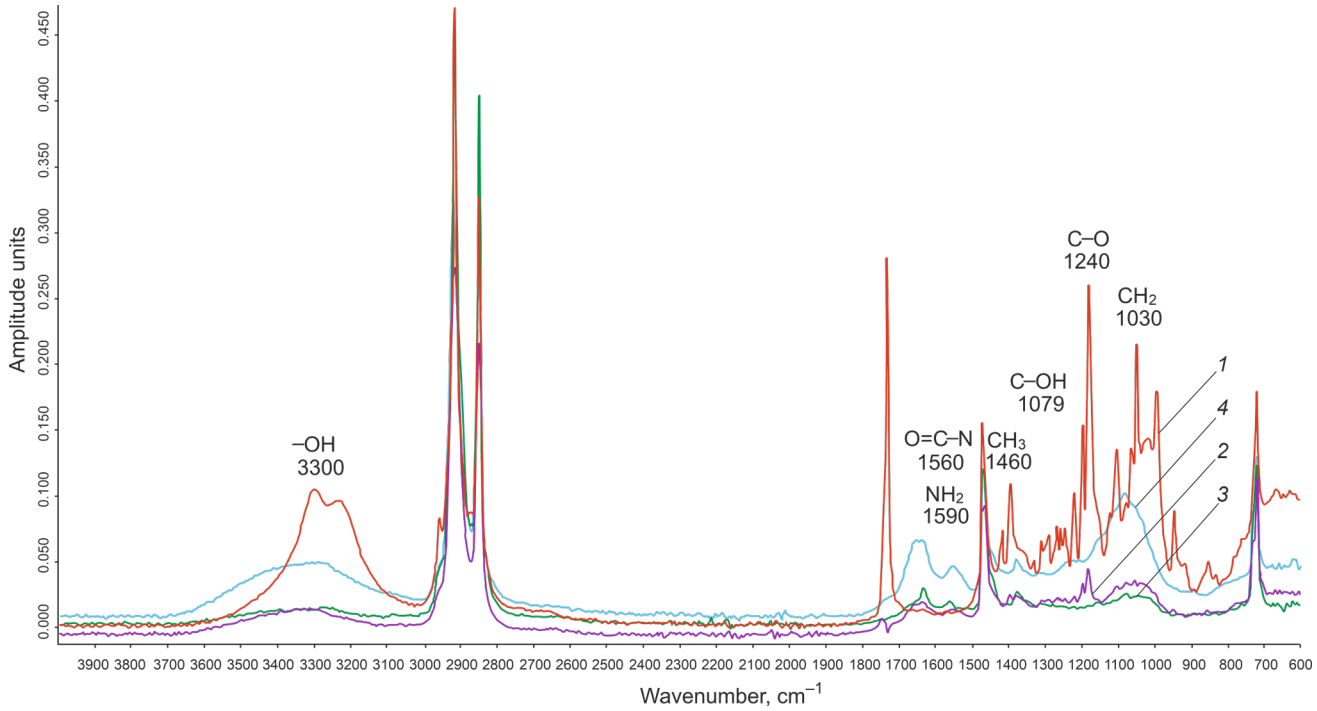

Fig. 2. Infrared spectrum of the BHC based on rice starch.
Red line (*1*) is the BHC absorption spectrum before biodegradation; violet line (*2*) is the BHC spectrum after one month of biodegradation; green line (*3*) is the BHC spectrum after three months of biodegradation; blue line (*4*) is the BHC spectrum after six months of biodegradation.

presence of the C–OH group, and 1500–1700 cm^{-1}, designating the presence of the acetamide groups O=C–N and amine groups NH_2. Thus, their appearance can be associated with the action of active microorganisms of the chitosan fungi group, which form the bacterial microflora. In the region of 3000–3600 cm^{-1}, changes in the intensity of the absorption peaks of the OH groups were observed. This is presumably due to the fact that TPS destroys the polymer matrix to some extent; most likely, TPS is partially washed out of the composition by water. This also supports the conclusion that the occurring biodegradation processes are intensive.

CONCLUSIONS

The process of the biodegradation of BHC compositions based on LDPE and TPS of various origins: corn, pea, and rice, with a TPS content in BHC from 40:60 wt % using the novel DMG plasticizer was studied. Biodegradation was carried out in biohumus for six months with periodic evaluation of the properties of control and working samples: following one month, three months, and six months.

It follows from the results of the experiment that the new modifier introduced into the samples composition increases the water absorption of the filled compositions in the case of BHC based on corn TPS by 20%; in the case of BHC based on pea TPS—by 26%; in the case of BHC based on rice TPS—by 31%.

The observed 60% degradation in the physical and mechanical characteristics of the samples as compared to the initial values is apparently due to a change in the material structure: weakening of energy bonds, destruction of the polymer matrix, partial washing out of the components from the system.

The results of optical microscopy and analysis carried out by FTIR confirmed the occurrence of sporulation of active microorganisms.

The obtained data support the conclusion that TPS can be used with the novel DMG plasticizer as a polyolefin modifier for the creation of biodegradable packaging materials.

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Authors' contribution

All authors equally contributed to the research work.

The authors declare 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

2. Kalia S. *Biodegradable Green Composites*. John Wiley & Sons; 2016. 368 p.

3. Anan'ev V.V., Kulikov P.P., Vasil'ev I.Yu. Study of polyolefin compositions capable of degradation. *Packaging*. 2015;(3):46–48 (in Russ.).

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. *Journal of Saudi Chemical Society*. 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*. 2016137:452–458. 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. In: *Biodegradable polymers as packaging materials. 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

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

2. Kalia S. *Biodegradable Green Composites*. John Wiley & Sons; 2016. 368 p.

3. Ананьев В.В., Куликов П.П., Васильев И.Ю. Исследование полиолефиновых композиций, способных к разложению. *Packaging*. 2015;(3):46–48.

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. *Journal of Saudi Chemical Society*. 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*. 2016137:452–458. 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. In: *Biodegradable polymers as packaging materials. 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. Tabasum S., Younas M., Zaeem M.A., Majeed I., Majeed M., Noreen A., NaeemIqbal 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

15. Wasserman L.A., Papakhin A.A., Borodina Z.M., *et al*. Some physico-chemical and thermodynamic characteristics of maize starches hydrolyzed by glucoamylase. *Carbohydr. Polym*. 2019;112:260–269. https://doi.org/10.1016/j.carbpol.2019.01.096

16. Kwon S.S., Kong B.J., Park S.N. Physicochemical properties of pH-sensitive hydrogels based on hydroxyethyl cellulose-hyaluronic acid and for applications as transdermal delivery systems for skin lesions. *Eur. J. Pharm. Biopharm.* 2015;92:146–154. https://doi.org/10.1016/j.ejpb.2015.02.025

17. Razavi S.M.A., Cui S.W., Ding H. Structural and physicochemical characteristics of a novel water-soluble gum from Lallemantia royleana seed. *Int. J. Biol. Macromol*. 2016;83:142–151. https://doi.org/10.1016/j.ijbiomac.2015.11.076

18. Lukin N.D., Kolpakova V.V., Usachev I.S., Sardzhvelazhdze A.S., Solomin D.A., Vasilyev 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 and Development Prospects: Proceedings of the International Congress*). 2019. P. 102–104 (in Russ.).

19. Kolpakova V.V., Usachev I.S., Sardzhveladze A.S., Solomin D.A., Ananiev V.V., Vasil'ev I.Yu. Perfection of technology of application of thermoplastic starch for biodegradable polymer film. *Pishchevaya promyshlennost' = Food Industry*. 2017;(8):34–38 (in Russ.).

20. Ananyev V.V., Nagornova I.V., Bablyuk E.B., Vasilyev I.Y., Varepo L.G. Polymer composites including natural additives degradation rate indication. In: AIP *Conference Proceedings*. 2017;1876(1):020091. https://doi.org/10.1063/1.4998911

21. Lukin N.D., Kolpakova V.V., Usachev I.S., Papakhin A.A., Sardzhveladze A.S., Borodina Z.M., Vasilev I.Yu., Ananev V.V. *Biologicheski razrushaemaya termoplastichnaya kompozitsiya* (*Biologically degradable thermoplastic composition*): Pat. RF 2691988. Publ. 19.06.2019. (in Russ.).

22. 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. *Fine Chem. Technol.* 2020;15(6):44–55 (in Russ.). https://doi.org/10.32362/2410-6593-2020-15-6-44-55

23. 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

24. Kolpakova V., Usachev I., Papakhin A., Sardzhveladze A., Ananiev V. Thermoplastic composition with modified porous corn starch of biodegradability properties. In: 2019 *Proceedings of the GEOLINS International Scientific Conference on Geosciences*. March 26–29, 2019. Athens, Greece. P. 33–41. https://doi.org/10.32008/geolinks2019/b2/v1/04

14. Tabasum S., Younas M., Zaeem M.A., Majeed I., Majeed M., Noreen A., NaeemIqbal 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

15. Wasserman L.A., Papakhin A.A., Borodina Z.M., *et al.* Some physico-chemical and thermodynamic characteristics of maize starches hydrolyzed by glucoamylase. *Carbohydr. Polym*. 2019;112:260–269. https://doi.org/10.1016/j.carbpol.2019.01.096

16. Kwon S.S., Kong B.J., Park S.N. Physicochemical properties of pH-sensitive hydrogels based on hydroxyethyl cellulose-hyaluronic acid and for applications as transdermal delivery systems for skin lesions. *Eur. J. Pharm. Biopharm*. 2015;92:146–154. https://doi.org/10.1016/j.ejpb.2015.02.025

17. Razavi S.M.A., Cui S.W., Ding H. Structural and physicochemical characteristics of a novel water-soluble gum from Lallemantia royleana seed. *Int. J. Biol. Macromol*. 2016;83:142–151. https://doi.org/10.1016/j.ijbiomac.2015.11.076

18. Лукин Н.Д., Колпакова В.В., Усачев И.С., Сарджвелаждзе А.С., Соломин Д.А., Васильев И.Ю. Модификация полимерных композиций с термопластичным крахмалом для биоразлагаемой упаковочной пленки. В: *Биотехнология: состояние и перспективы развития: Материалы международного конгресса*. 2019. С. 102–104.

19. Колпакова В.В., Усачев И.С., Сарджвеладзе А.С., Соломин Д.А., Ананьев В.В., Васильев И.Ю. Совершенствование технологии применения термопластичного крахмала для биоразлагаемой полимерной пленки. *Пищевая промышленность*. 2017;(8):34–38.

20. Ananyev V.V., Nagornova I.V., Bablyuk E.B., Vasilyev I.Y., Varepo L.G. Polymer composites including natural additives degradation rate indication. In: *AIP Conference Proceedings*. 2017;1876(1):020091. https://doi.org/10.1063/1.4998911

21. Лукин Н.Д., Колпакова В.В., Усачев И.С., Папахин А.А., Сарджвеладзе А.С., Бородина З.М., Васильев И.Ю., Ананьев В.В. *Биологически разрушаемая термопластичная композиция*: Пат. 2691988 РФ. Заявка № 2018146738; заявл. 26.12.2018. опубл. 19.06.2019.

22. 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

23. 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

24. Kolpakova V., Usachev I., Papakhin A., Sardzhveladze A., Ananiev V. Thermoplastic composition with modified porous corn starch of biodegradability properties. In: *2019 Proceedings of the GEOLINS International Scientific Conference on Geosciences*. March 26–29, 2019. Athens, Greece. P. 33–41. https://doi.org/10.32008/geolinks2019/b2/v1/04

25. Васильев И.Ю., Ананьев В.В., Султанова Ю.М., Колпакова В.В. Влияние состава биоразлагаемых композиций на основе полиэтилена, крахмала и моноглицеридов на их физико-механические свойства и структуру. *Все материалы. Энциклопедический справочник*. 2021;(5):31–38. https://doi.org/10.31044/1994-6260-2021-0-5-31-38

25. Vasilyev I.Yu., Ananyev V.V., Sultanova Yu.M., Kolpakova V.V. Composition effect of biodegradable compounds based on polyethylene, starch and monoglycerides on their physical-mechanical properties and structure. *Vse materialy. Entsiklopedicheskii spravochnik* (*All Materials. Encyclopaedic Reference Manual*). 2021;(5):31–38 (in Russ.). https://doi.org/10.31044/1994-6260-2021-0-5-31-38

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