SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

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RESEARCH ARTICLE

Development of technology for producing biodegradable hybrid composites based on polyethylene, starch, and monoglycerides

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Objectives. *This work aimed to develop technology to produce biodegradable hybrid composite (BHC) films based on low-density polyethylene (LDPE) 115030-070 and thermoplastic starches (TPS) of various origins (corn, pea, and rice), with distilled monoglycerides as the plasticizer. The properties of the produced BHC films were studied and the optimal native starch : glycerol : monoglycerides ratio is proposed.*

Methods. *TPS and BHC films based on this material were produced from different types of native starches in laboratory extruders (Brabender and MashPlast, Russia), and the extruded melts were subjected to ultrasonic vibrations. The structure and appearance of the BHC films were studied using scanning electron microscopy and rheology. Their biodegradability was assessed by immersing them in biocompost for three months. To evaluate the mechanical performance of the BHC films produced with and without ultrasound, the changes in tensile stress and elongation at break were determined during the biodegradation process.*

Results. *The BHC films had a homogeneous structure, except small agglomerates (non-melted starch grains), which did not reduce their quality. The films with monoglycerides had high tensile strength, which was comparable with low-density polyethylene. After removing samples of the BHC films from the biocompost, their tensile strength decreased by 20%, which shows their biodegradability.*

Conclusions. *The produced biodegradable composite films and the technology used to produce them will be applicable for the packaging industry to reduce environmental impact.*

Keywords: *polyolefin, thermoplastic starch, biodegradable polymer composite, structural modification, extrusion*

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НАУЧНАЯ СТАТЬЯ

Разработка технологии получения биоразлагаемых композиций на основе полиэтилена, крахмала и моноглицеридов

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Цель. *Совершенствование технологии создания биологически разрушаемых гибридных композиций (БГК) на основе полиэтилена низкой плотности (ПЭНП) 11503-070 и термопластичных крахмалов различного происхождения (кукурузы, гороха, риса) с новыми пластификаторами – моноглицеридами дистиллированными. Разработка технологической схемы производства БГК. Получение и исследование свойств биологически разрушаемых композиционных пленок, пластифицированных смесью дистиллированных моноглицеридов и глицерина. Выбор оптимального соотношения нативный крахмал : глицерин : моноглицериды.*

Методы. *Термопластичный крахмал и композиционные пленки получали на основе нативных крахмалов разных видов в лабораторных экструдерах фирм «Брабендер» и «МашПласт» (Россия), при этом экструдируемый расплав композиции подвергали воздействию ультразвуковых колебаний. Была изучена структура композитных пленок методом сканирующей электронной микроскопии, а также их реологические характеристики. Проведена оценка органолептических свойств композитных пленок. Способность к биоразложению композитных пленок оценивали при помощи погружения их на три месяца в биогумус. Для оценки эксплуатационных свойств БГК, до и после процесса биоразложения, определяли разрушающее напряжение при растяжении и относительное удлинение при разрыве, причем оценка была проведена и для пленок, которые подвергали воздействию ультразвука.*

Результаты. *Был достигнут положительный эффект от использования нового пластификатора – дистиллированных моноглицеридов в композициях термопластичный крахмал : полиэтилен. При производстве композиции получались однородными по структуре, иногда образовывались небольшие агломераты, представляющие собой нерасплавившиеся частицы крахмала, что не ухудшало качество готовых БГК. Композиты с моноглицеридами обладали высокой прочностью на разрыв – практически на одном уровне с ПЭНП. После изъятия образцов композитных пленок из биогумуса их прочность на разрыв снижалась на 20%, что свидетельствует о протекании процесса биоразложения.*

Выводы. *Разработанный состав и технология получения биологически разлагаемых композитных пленок могут быть использованы в дальнейшем для производства композитных пленок с высоким содержанием крахмала для применения в упаковочной отрасли, что позволит снизить негативную нагрузку на окружающую среду.*

Ключевые слова: *полиолефины, термопластичный крахмал, биоразлагаемые полимерные композиции, структурная модификация, экструзия*

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INTRODUCTION

Recently, the rapid growth in the consumption of synthetic plastics in many sectors of the economy, especially in the field of packaging, has been a major concern. Plastic containers are used for packaging food products, medicines, electronic devices, liquids, some of which have an increased hazard class [1]. According to the German research institute, *Nova-Institute*[1], which deals with polymer technologies, global plastic production in 2019 reached almost 400 million tons, whereas the volume of biodegradable plastics obtained from renewable resources was only 3.5 million tons, i.e., approximately 1% of the total production[2] [2]. Since only 25% of plastic wastes are recyclable, there is a need to create biodegradable polymer compositions [3–5]. This issue has economic and environmental facets because it is associated with the need to reduce the cost of raw materials for the production of various products, and ensure environmental protection [6–10].

Some technologies for producing biodegradable polymer hybrid composites (BHCs) and products based on them are presented in [11–15]. One of the most promising approaches to produce BHCs is the use of thermoplastic starch (TPS) as the main component [16, 17]. To obtain TPS, native starch is mixed with various plasticizers by heating [18, 19]. The use of TPS instead of native starch as a filler for polyolefin compositions allows for more effective processing and higher thermal stability of the finished compositions [20–22]. The TPS content in the compositions can be as much as 40–60 wt % [8, 9]. Therefore, the purpose of this work is to improve the technology for producing BHCs, containing distilled monoglycerides (DMG) and intended for use as packaging materials, select the optimal technological parameters, and develop a basic technological scheme for their production.

MATERIALS AND METHODS

Low-density polyethylene (LDPE) (Grade 11503-070), produced by *Kazanorgsintez* (Russia), and composite materials based on it, filled with starch-containing products, were used. The average molecular weight of the LDPE was 1.8×10^4. PC-94 glycerin with a density of 1.24 g/cm^3, produced by *TC Vympel* (Russia) and issued in accordance with GOST 6824-96, and DMG produced according to technical specifications TU 10-1197-95 by *Rushimtrade* (Russia) were also used. Corn starch produced by *Krakhmaloprodukt* (Orel, Russia) in accordance with GOST 32159-2013, rice starch—*Vinh Thuan Trading Import-Export Co. Ltd* (Vietnam), and pea starch—*Roquette* (France) were used as filler for LDPE. The grain size and gelatinization temperature of these starches are shown in Table 1.

TPSes of different species were produced based on the native starches in laboratory extruders provided by *Brabender* (Germany) and *MashPlast* (Russia) firms. To do this, starch, glycerol, and DMH were mixed for 20–30 min in the dispersant. The resulting mass was loaded into the extruder and processed into a rod (strand) at extruder outlet temperatures from 115°C to 140°C. The TPS strands were cooled and crushed using a granulator to produce granules from 2 to 4 mm in size. These granules were used for the production of the BHC films through mixing with LDPE in a laboratory flat-die extruder manufactured by *MashPlast* (Russia).

The melt flow rate (MFR) of the films was determined using an IIRT-5 capillary viscometer (*TOCHMASHPRIBOR*, Russia) at a ratio of 60 : 40 of TPS to LDPE mass fractions, a temperature of 190°C, and a load of 2.16 kg.

The mechanical properties of samples of the films under tension were determined using a RM-50 testing machine manufactured by *MashPlast* (Russia) equipped with a computer interface with

Table 1. Properties of native starches

Property	Native starch type		
	Corn	Rice	Pea
Grain size, μm	5–25	8–32	7–30
Gelatinization temperature, °C	62–72	68–78	57–70

[1] URL: http://nova-institute.eu/.

[2] Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2019 – 2024. Hürth, Germany: Michael Carus (V.i.S.d.P.); 2020. URL: http://bio-based.eu/downloads/bio-based-building-blocks-and-polymers-global-capacities-production-and-trends-2019-2024/

the StretchTest software (Russia). The tensile stress and elongation at break of the films were measured at a temperature of 23 ± 2°C and a relative humidity of 50 ± 5% according to the method described in GOST 14236-81. The limit of the permissible load measurement error did not exceed ±1%. The maximum deviation in the width of the samples was ± 0.2 mm. The average value was determined over 3–5 measurements. The tests were performed at a strain rate of 100 mm/min. Samples of the films for testing were obtained using a cutting device, with the shape of the samples corresponding to type 1B (ENISO 527-3).

To assess the biodegradation dynamics of the filled polymer compositions, the composting method was used. The samples were placed in special trays with biocompost at a temperature of 23 ± 2°C and a humidity of 70 ± 10%, and kept there for 3 months. The degree of biodegradation of the films was evaluated by assessing changes in their physical and mechanical properties i.e., breaking stress at tension (σ) and elongation at break (ε), according to GOST 54530-2011.

The surface morphology of the films was studied using a high-resolution, autoemission, scanning electron microscope, JSM-7500F (*JEOL*, Japan).

RESULTS AND DISCUSSION

Dry native starch, in accordance with the scheme shown in Fig. 1, was loaded into the container of a laboratory dispersant, which was fed glycerol and DMH plasticizer through a dispenser to achieve a ratio of 60 : 30 : 10 [10]. Native starch, glycerol, and plasticizer were thoroughly mixed for 20–30 min at a speed of 70 rpm. Here, a homogeneous paste-like mass was obtained. The following steps were performed to produce the TPS:

– dosage of the TPS components: native starch, glycerol and plasticizer;
– pre-mixing of the native starch, glycerol and plasticizer;
– extrusion of the TPS composition;
– cooling of the TPS extrudate;
– pelletizing of TPS and
– packaging of the finished granulate TPS.

The mixture in the extruder was heated, plasticized, and then pressed through the cylindrical holes of the extruder head. The resulting strands were cooled and crushed into granules of 2–4 mm in size at a speed of 120 rpm. The TPS granules were dried in a vacuum cabinet at a temperature of 60°C.

The technological scheme for the manufacture of TPS is shown in Fig. 1.

To select the relevant modes of extrusion production of the BHC films, the rheological properties of the compositions, in particular, MFR, were studied. The results are given in Table 2. It can be seen that the viscosity of the BHC film melts at the maximum TPS : LDPE mass ratio of 60 : 40 increased and the MFR of the films decreased by 20.0–27.1% compared with the original LDPE, which is likely due to the agglomeration of starch particles in the melt during the formation of the BHC structure. The minimum value of MFR was observed in the BHC film made from rice starch. This reduction in MFR can lead to a slight decrease in the productivity of extrusion equipment in the manufacture of such compositions.

The obtained TPS granules based on different types of starches were mixed with LDPE in a laboratory twin-screw extruder equipped with an ultrasonic melt processing unit at TPS : LDPE ratios ranging from 40 : 60 to 60 : 40, and BHC was obtained in the form of strands under the temperature conditions, shown in Table 3.

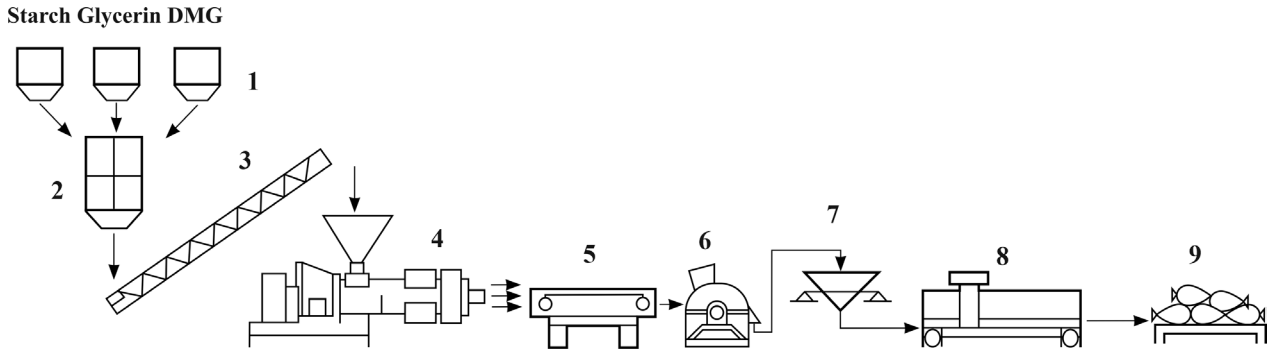


Fig. 1. Technological scheme for the manufacture of TPS:
(1) loading hopper, (2) disperser, (3) screw conveyor, (4) extruder, (5) cooling bath, (6) granulating device, (7) scales, (8) bag sewing machine, and (9) finished products.

Table 2. Melt flow rate (MFR) of the initial LDPE and LDPE-based BHC films

No.	Compositions	MFR, g/10 min
1	Original LDPE	7.0 ± 0.2
2	BHC (TPS with pea starch)	5.6 ± 0.1
3	BHC (TPS with corn starch)	5.4 ± 0.3
4	BHC (TPS with rice starch)	5.1 ± 0.2

Table 3. Temperature ranges of BHC production

BHC type	Cylinder zone temperature, ℃				
	Zone of the extruder				
	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5
BHC based on corn TPS	110	125	135	140	140
BHC based on pea TPS	110	120	125	130	130
BHC based on rice TPS	110	115	120	125	125

The diameter of the extruder screws was 16 mm. The speed of the screws was 60–80 rpm. The strands were cut into granules of approximately 2 mm in size at a knife speed of 140–160 rpm.

A schematic diagram of the used twin-screw extruder apparatus is shown in Fig. 2.

Then, the granules obtained using the twin-screw extruder were loaded into a laboratory single-screw extruder with a screw diameter of 12 mm, which was also equipped with an ultrasonic melt processing unit, and extruded through a flat-slot head with a width of 130 mm. A barrier screw was used, which during the extrusion process ensured homogenization of the LDPE/TPS mixture and high quality of the polymer film. The speed of rotation of the screw varied from 70 to 90 rpm.

The mass coming out of the head was transferred to cooled receiving shafts, stretched using a broaching device, and rolled, resulting in the BHC film.

A schematic diagram of the flat-slot single-screw extruder is shown in Fig. 3.

In the manufacture of the BHC films, the polymer melt was exposed to ultrasonic vibrations, and processed by ultrasound directly in the extruder using an ultrasonic attachment, which was a magnetostrictive converter with a titanium waveguide. To remove heat from the ultrasonic attachment, a water jacket was used. A schematic diagram of the ultrasonic attachment is shown in Fig. 4.

The ultrasonic attachment was installed between the screw zone and the extrusion head. The waveguide of the ultrasonic attachment was immersed directly in the melt. The attachment was equipped with an oscillator with a frequency of 22 kHz, and the oscillation amplitude of the waveguide end was up to 10 μm. In the manufacture of the BHC film, a frequency of 22 kHz and power up to 1.0 kW was used for melt processing. With a higher power of the ultrasonic unit, the melt began to foam when leaving the flat-slot head due to the destruction of the polymer composition, resulting in through holes in the film.

After BHCs were obtained in the form of polymer films, their organoleptic characteristics were determined.

The appearance of the BHC film samples prepared from the maximum achievable TPS : LDPE ratio is shown in Fig. 5.

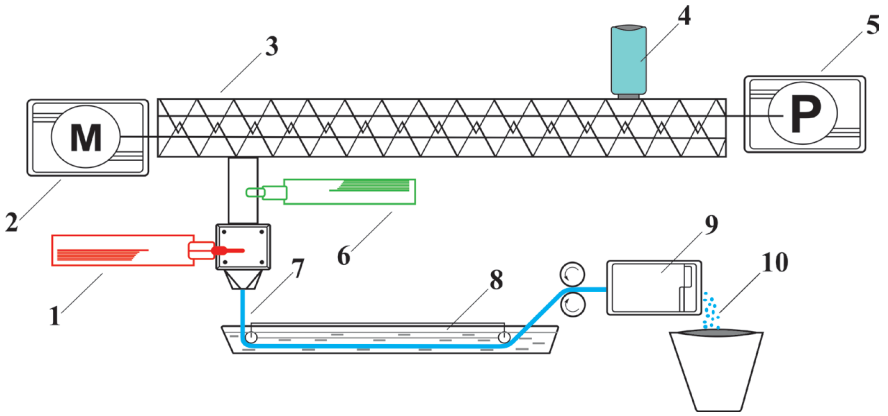


Fig. 2. Schematic of the twin-screw extruder for obtaining composite granules:
(1) ultrasonic attachment, (2) engine, (3) twin-screw extruder, (4) loading hopper, (5) gearbox synchronized with the engine, (6) pressure sensor, (7) strand, (8) cooling bath, (9) granulator, and (10) composite granules.

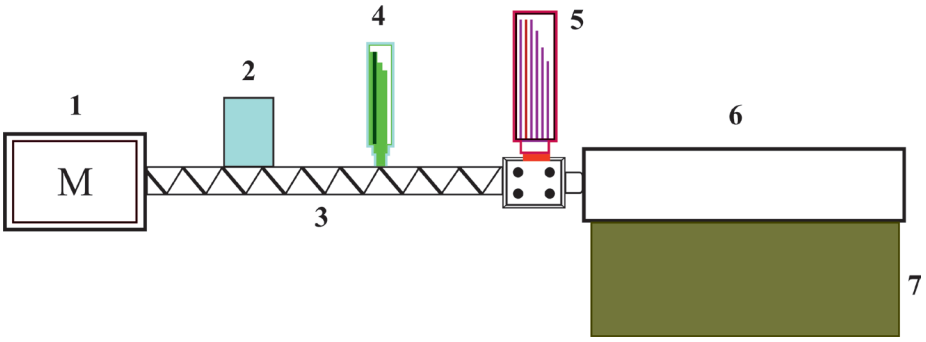


Fig. 3. Schematic of the flat-slot single-screw extruder:
(1) engine, (2) loading hopper, (3) screw, (4) pressure sensor, (5) ultrasonic attachment, (6) flat-slot head, and (7) melt of the finished composite.

The films produced at the maximum achievable TPS : LDPE ratio with the three types of TPS had a uniform matte-white surface without agglomerates in the form of non-melted starch particles, and no cracks or other damage. This indicates that homogenization of the compositions was achieved.

Although the initial assessment of the organoleptic properties of the finished BHC films showed positive results, it was important to consider the structural changes in the BHC films. As an example, Fig. 6 shows micrographs of the BHC films obtained at the maximum TPS : LDPE ratio of 60 : 40, based on rice starch.

Figure 6a shows agglomerates of thermoplastic starch, some with a “grain” phase interface, while Fig. 6b showed oriented structures formed in the film composition.

For BHC to be used as a raw material for polymer packaging, it is important to achieve high mechanical performance. For this purpose, the following mechanical characteristics of the BHC films were studied: breaking stress at tension (σ) and elongation at break (ε). The test results are shown in Table 4.

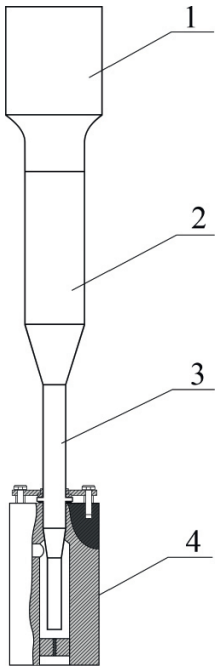


Fig. 4. Schematic of the ultrasonic attachment:
(1) transducer of ultrasonic vibrations, (2) concentrator (waveguide), (3) emitter, and (4) extrusion head.

As can be seen from the test results, the BHC films demonstrated high strength, almost at the level of LDPE, and strong deformation characteristics, which makes BHC applicable for use in packaging.

Furthermore, the effect of ultrasonic vibrations on the melt for all compositions improved both strength and deformation indicators, which shows that the compositions were homogenous and that there was an increase in the interaction between the polymer matrix of polyethylene and TPS of various origins.

a b c

Fig. 5. Appearance of representative BHC film samples with a TPS : LDPE ratio of 60 : 40, using (a) corn TPS, (b) pea TPS, and (c) rice TPS.

The resulting compositions were tested for the possibility of biodegradation by placing the film samples in biocompost. In the production of polymer film materials, it is of great importance to ensure that a certain value of breaking stress at tension and elongation at break is achieved, as well as to maintain these indicators within acceptable limits during operation. Moreover, the appearance of the films is preserved when in contact with the environment. To simulate the long-term operation of the films, they were immersed in biocompost with active microorganisms for 3 months. After removing the samples from the biocompost, their destructive tensile strength and relative elongation at break were measured. The test results are shown in Table 5.

On analyzing the data in Table 5, it can be noted that the mechanical properties of the film samples changed after 3 months of storage in a biocompost, and these changes happened faster for samples subjected to ultrasonic treatment. The decrease in strength of the BHC films based on corn, pea and rice starch without ultrasound was 1.2, 1.3, and 1.6 times, respectively, and the decrease in strength of the BHC films based on corn, pea and rice starch with ultrasound was 1.5, 1.5, and 1.7 times, respectively. We can conclude that the biodegradation period would be shorter in the recycling of such films.

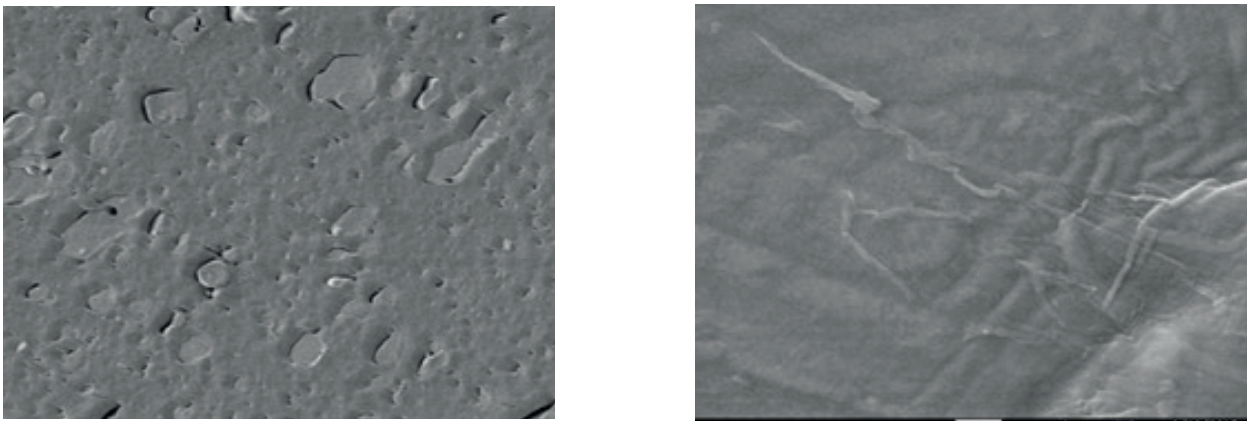
CONCLUSIONS

Films have been produced from biologically degradable hybrid composite material based on LDPE and TPS, with the addition of DMG as the plasticizer component.

Laboratory samples of the BHC films based on different ratios of LDPE and TPS of various types: corn, pea and rice from 40 : 60 to 60 : 40 wt %, with the addition of DMG plasticizer with and without the use of ultrasound were produced using flat-panel extrusion.

The optimal native starch/glycerol/DMG ratio was established to be 60 : 30 : 10 wt %.

MFR of the BHC films were measured. The BHC film with a maximum mass fraction of 60%



a b

Fig. 6. SEM micrographs of the BHC films based on a TPS : LDPE ratio of 60 : 40 under a magnification of (a) 500×, and (b) 10000×.

Table 4. Physical and mechanical properties of BHC films

No.	TPS : LDPE ratio	σ, MPa (Δ ± 0.2)	ε, % (Δ ± 5)	σ, MPa (Δ ± 0.2)	ε, % (Δ ± 5)
1	LDPE only	13	115	–	
–		**With DMG without US exposure***		**With DMG and US exposure***	
2	**Corn-based TPS**				
	60 : 40	9.8	62	10.9	78
	50 : 50	10.4	68	11.6	84
	40 : 60	11.4	72	12.8	93
3	**Pea-based TPS**				
	60 : 40	6.7	68	7.8	82
	50 : 50	7.8	73	9.3	91
	40 : 60	8.9	78	10.1	102
4	**Rice-based TPS**				
	60 : 40	10.4	74	11.2	96
	50 : 50	10.9	79	11.9	104
	40 : 60	11.6	93	12.8	115

* *Note:* US is ultrasound.

Table 5. Physical and mechanical properties of BHC films in biocompost

No.	TPS : LDPE ratio	σ, MPa (Δ ± 0.2)	ε, % (Δ ± 5)	σ, MPa (Δ ± 0.2)	ε, % (Δ ± 5)
		With DMG without US exposure*		**With DMG and US exposure***	
1	**Corn-based TPS**				
	60 : 40	8.1	49	7.1	47
	50 : 50	8.4	56	7.6	53
	40 : 60	9.4	68	8.8	64
2	**Pea-based TPS**				
	60 : 40	5.3	52	5.1	50
	50 : 50	7.6	64	5.9	62
	40 : 60	8.3	70	6.6	68

Table 5. Continued

No.	TPS : LDPE ratio	σ, MPa (Δ ± 0.2)	ε, % (Δ ± 5)	σ, MPa (Δ ± 0.2)	ε, % (Δ ± 5)
		With DMG without US exposure*		With DMG and US exposure*	
3	Rice-based TPS				
	60 : 40	6.3	43	6.0	41
	50 : 50	7.3	55	6.7	53
	40 : 60	9.3	70	7.8	67

* *Note:* US is ultrasound.

TPS, showed an increase in melt viscosity by up to 60%. This may reduce the productivity of process equipment in the production of BHC films.

A technological scheme for manufacturing TPS for the production of BHC with DMG plasticizer under the influence of ultrasonic vibrations is proposed.

The structural properties of the obtained BHC films were studied. It is shown that the addition of the DMG plasticizer to the BHC films has a favorable effect on the properties of the films.

The mechanical properties of the BHC films were also evaluated. It is shown that the effect of ultrasonic vibrations on the melt in the manufacture of the films improves the mechanical properties, as well as accelerates their biodegradation.

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Authors' contribution

I.Yu. Vasilyev – conducting the study, collection and provision of the material, writing the article;

V.V. Ananyev – planning the experiment, scientific editing.

The rest of the authors equally contributed to the experiment, writing, and design of the article.

The authors declare no conflicts of interest.

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