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IMPROVEMENT OF PRODUCTION TECHNOLOGY FOR THERMOPLASTIC COMPOUNDS INTENDED FOR THE PRODUCTION OF BIODEGRADABLE POLYMER MATERIALS

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A B S T R A C T

The article presents the preparation and study of the properties of thermoplastic compounds based on a new glycerol/monoglyceride plasticizing system instead of the traditionally used glycerol/sorbitol in mixtures with native starch (corn, pea, rice) to obtain biodegradable polymer compositions. By mixing starch/glycerin/monoglyceride and starch/glycerin/sorbitol alternately, they were processed in a Mash-Plast laboratory twin-screw extruder (Russia) and produced thermoplastic compounds in the form of round-section strands and granules. When using a new plasticizing system based on glycerin/monoglyceride instead of the traditionally used glycerin/sorbitol in the process of manufacturing thermoplastic compounds in mixtures with starch of various origins (corn, pea, rice) during extrusion, a more homogeneous monolithic structure is formed, which has an effect on increasing the strength properties by two times compared to the use of a glycerin/sorbitol plasticizing system, in which the formation of a more defective structure with a phase boundary between the starch-sorbitol components was observed. When determining the thermophysical properties and supramolecular structure of thermoplastic compounds, it was established that starch is characterized by different proportions of amylose and amylopectin, which affects the temperature of their processing with sorbitol and monoglyceride plasticizers. It has been shown that the conversion of native starch into a thermoplastic state using a new plasticizing system with monoglyceride, as in the case of sorbitol, is accompanied by a change in the phase state, resulting in the decrystallization of the initial starch, which affects the production of homogeneous composite melts with the possibility of their processing by extrusion.

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1. INTRODUCTION

The increase in the production of polymer products is associated with the problem of waste generation, which requires scientifically sound approaches to its disposal and recycling. One of the practical ways to reduce polymer waste is the development of biodegradable polymer materials (Guivan et al., 2024).

There are several approaches to the creation of biodegradable polymer materials: synthesis of polymers from renewable raw materials, for example, polylactide (PLA), polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS), and others (Brovina et al., 2024; Kalia, 2016); the use of natural polymers after mechanical and/or chemical processing, for example, polysaccharides – cellulose, starch, arabinogalactan (Carus, 2020); application of fillers with functional groups that initiate decomposition under the action of photo- or oxo-degradation – amphiphilic polymer metal complexes, pro-oxidant additives (Nishat & Malik, 2016; Sudhakar & Selvakumar, 2012); modification of synthetic thermoplastic polymers with fillers from renewable raw materials (Mendes et al., 2016) and/or natural polymers (Nguyen et al., 2016; Tang & Alavi, 2011).

Given the existing approaches to the production of biodegradable polymer materials, one of the most accessible and simple methods to date is the modification of synthetic polymers with fillers of natural origin (Singh et al., 2021; Gomes et al., 2025).

In this regard, the production of compositions based on synthetic polymers filled with starch appears to be promising (Ojogbo et al., 2020). It should be noted that the biodegradability kinetics of polymer composites depends not only on the nature of the filler used, but also on its concentration in the composites, which determines the prospects for its use, but at the same time affects the reduction of operational properties, which affects the consumer properties of finished products (Tudorachi et al., 2000; Fonseca-García et al., 2021). The introduction of a filler of more than 30 wt% (Mittal et al., 2020; Aleksanova et al., 2023) causes the dispersed modifier to agglomerate due to the high surface energy between its particles. It is also necessary to take into account the dispersibility of the initial filler particles: as the particle size decreases, their specific surface area in the polymer system increases sharply, which affects the technological difficulties of manufacturing biodegradable polymer materials when they are used, associated with the occurrence of defects in the form of "through holes" in the process of molding products, for example, from polymer melts during extrusion. In this regard, biodegradable compositions based on dispersion-filled systems must have an optimal particle concentration that ensures maximum modification of the polymer matrix properties (Ashori & Kuzmin, 2024).

Starch is a natural polysaccharide found in various plant organs and their fruits. It is produced in large quantities worldwide and is used in the food, pharmaceutical, paper, and other industries. In Russia, starch is mainly produced from corn, potatoes, wheat, barley, sorghum, peas, rice, and rye (Kuzmin et al., 2023). Depending on its origin, starch-containing raw materials are characterized by different particle size distributions, which is important to consider in the technological process of manufacturing biodegradable polymer compositions.

Starch is a product of photosynthesis: it is formed by plants absorbing light energy and assimilating carbon dioxide and water. Starch is a polymer of glucose, which is formed and exists in various forms. The predominant form is the cyclic pyranose form. The conversion of the open form of D-glucose into cyclic α-D-glucose is accompanied by the formation of an oxygen bridge -O- between the first and fourth carbon atoms. In the structure of native starch, the most reactive group is the hydroxyl (-OH-) group at the 6th carbon atom, which attaches the side chains of polysaccharides.

The polymerization of glucose molecules is a complex biochemical process that mainly occurs with the formation of a supramolecular structure consisting of amylose and amylopectin. Amylopectin has a branched (amorphous) structure and consists of the same glucose residues as amylose (mainly α-1,4-D-bonds), which is characterized by a linear structure but also has side chains attached at branch points via α-1,6-bonds.

The main enzyme acting in several isoforms in the formation and development of starch crystallites is GBSS (granule-bound starch synthase). The enzymes SSS, SBE, and SDBE are also involved in this process, which is why the mechanism of grain formation with different ratios of amylose and amylopectin, crystalline and amorphous parts, is extremely complex. The idea of the formation of double helices of amylose chains and cluster (bunch) amylopectin formations in starch was developed by D. French. According to his theory, starch biosynthesis occurs on the surface of the grains, and the amylose and amylopectin molecules are oriented perpendicular to it and in opposite directions. Thus, the reducing end is located on the surface of the grains in amylose, while in amylopectin, on the contrary, the non-reducing ends are located there, which can further branch and elongate with the SBE enzyme. In this case, the amylose chain is elongated by the action of the SSS enzyme, so amylose and amylopectin molecules are difficult to combine and can be fractionated under certain conditions. Native starch grains have growth rings, which are alternating layers of varying density, crystallinity, and resistance to chemical and enzymatic effects. The wide layers are formed as a result of the alternating filling and removal of molecules in plastids

with the sequential deposition of large insoluble and small soluble molecules; in this case, high-molecular-weight fractions of amylopectin prevail in the dense layers. The degree of crystallinity of starch grains varies between 14 and 42% and depends on the ratio of amylose to amylopectin content. Short chains in the amylopectin molecule form double helices, which form crystalline lamellae (crystallites). Free double helices and crystallites create semi-crystals.

The remaining amylose molecules and long amylopectin chains form the amorphous part of the starch grains. During the synthesis and crystallization of amylopectin, a small amount of phosphates remain bound to the hydroxyl group of the 6th carbon atom, their content in native starch reaches 0.2%. Amylose tends to capture lipids in the cytosol when forming spirals. The content of bound lipids in the starch of cereals and legumes is 0.2–1.3%.

During the formation and growth of starch grains in their crystalline part, the linear chains of amylose form single spirals with 6 glucose residues in each turn and create a Vh structure, while the side chains of amylopectin form double spirals with dense and sparse packing. Amylose and amylopectin form a structural complex of grains, which consists of crystalline and amorphous parts. In addition, within the layers themselves, amylopectin molecules have a rhythmic alternation of rows of clusters with a row thickness of 70Å (7 nm) and a layer thickness of about 2000-4000Å. In the crystalline part of amylopectin, each double helix has an inner diameter of 3.5Å, which prevents water molecules from fitting inside it; the outer diameter of the helix is 10.3Å. The double helices are connected into a large cluster with varying packing densities.

The length of the non-crystalline part of the branched amylopectin cluster is 20-22Å, while that of the crystalline part is 50-66Å. Overall, the length of the amylopectin molecule is 1200-4000Å and is an integral part of both structures—amorphous and crystalline. This model of starch crystallites was first proposed by A. Sarko and H. Wu. The latter type of packing is found in native wheat, rye, and pea starches, but is mainly formed during heat treatment and starch retrogradation. Native starch grains also contain mixed crystalline structures (A+B), called the C-form, which is characteristic of pea starch.

Different types of starch vary in both composition and amylose and amylopectin content. In native starch, it usually consists of 75-85% amylopectin and 15-25% amylose. However, there are plants in nature whose starch grains contain up to 100% amylopectin (waxy corn starch) and up to 75% amylose (high-amylose corn starch). The properties of starch depend not only on the ratio of amylose to amylopectin, but also on the degree and type of crystallinity of the starch grains.

The morphological and granulometric characteristics of starch grains in processed starch-containing raw materials are crucial for industrial starch production. The shape and size of grains significantly influence the choice of methods for extracting starch from plant raw materials. According to Stokes' law, the larger the grains, the faster they settle. Rye, wheat, and barley starch are characterized by a bimodal distribution of grains by size, expressed by the presence of two fractions: coarse-grained and fine-grained. This grain distribution affects not only the technological processes of their extraction, but also the structure, amylose content, thermodynamic and rheological characteristics of starch.

The type of starch and the corresponding grain size largely determine its structural order. Starch grains come in a wide variety of shapes: round, oval, lens-shaped, and polyhedral. Round and oval grains are characteristic of starches from root crops, peas, soft wheat, and floury corn varieties. The grains of durum wheat, waxy and silky corn, rice, and barley have a polyhedral and irregular shape. This is due to the conditions of grain formation and development: they are formed in a protein matrix at low humidity and are compressed during grain ripening.

The technological complexity of producing biodegradable polymer materials using polysaccharides is due to the fact that the native state of starch does not allow it to be processed under conditions similar to those used for thermoplastic polymers, since starch does not become viscous when heated, but rather decomposes (Tabasum et al., 2019). Another factor limiting the use of starch in mixtures with synthetic thermoplastics is the low interfacial interaction between the filler and the matrix polymer, which impairs their interaction at the supramolecular level. In this regard, various plasticizing components designed to improve the technological processability of binary systems are used to create biodegradable compositions based on thermoplastics filled with starch. One such component is glycerin.

Glycerin is a triatomic alcohol, one of the most common and affordable plasticizers used for polymers. When added to a binary mixture based on a polymer and filler, it improves the processability and thermal stability of polymer compositions based on them. However, due to their low molecular weight, glycerol molecules are capable of migrating to the surface of polymer products during use, which leads to starch retrogradation, causing thermoplastic starch to become brittle, which affects the reduction of the complex deformation-strength properties, and, as a result, to accelerated aging of finished products. To minimize the migration of glycerin to the surface of polymer compositions, its derivatives are used, in particular, monoglyceride.

Monoglycerides are esters, which are products of the substitution of one hydroxyl group in a glycerol molecule with a fatty acid molecule. Depending on the structure of the fatty acid, a large number of different monoglycerides with various physical and chemical properties can be obtained. Monoglycerides are widely used in the food, pharmaceutical, and perfume industries. In the food industry, monoglycerides are used as emulsifiers, stabilizers, complexing agents, and as substances that ensure the aggregate stability of food products. Monoglycerides are obtained by esterification of glycerol with fatty acids, as well as by glycerolysis of edible fats or oils. However, the reaction product is usually a mixture of mono-, di-, and triglycerides, glycerol, and free fatty acids.

In this regard, the Laboratory for the Development and Use of Synthetic and Natural Polymers and Composites at the Department of Innovative Materials for the Print Media Industry at Moscow Polytechnic University has developed a technology based on the use of a glycerol and sorbitol plasticizing system, which promotes the conversion of native starch into a thermoplastic state with the possibility of processing on extrusion equipment. However, it has been found that the above system is not suitable for all types of native starches, and therefore the scientific question of selecting components for the conversion of native starch into a thermoplastic state, which will improve the compatibility of the components with synthetic thermoplastic polymers, remains unresolved.

To assess the ability of polymer biocomposite materials to degrade biologically, methods corresponding to real conditions of degradation in the environment are used, as well as model experiments with a limited number of factors affecting the material. The most widely used methods for assessing the biodegradability of polymer materials are listed in Table 1.

Table 1. Methods for determining the biodegradation of polymer composite materials

No.	Method	Method essence	Standard
1.	Mycological test	Determination of material resistance to mold fungi cultures	ISO 846 ASTM G 21-90 ASTM G 21-96 GOST R IEC 60068 GOST 9.049-91
2.	Bacterial test	Determination of material resistance to bacterial cultures	ISO 846 ASTM G 22-76
3.	Biodegradability of insoluble substances (BODIS (BOD of insoluble chemicals))	Determination of the amount of oxygen absorbed during aerobic degradation of poorly soluble substances in a solid medium (4 months)	ISO 10708 OECD 301 D
4.	Test in free space at 25/50°C (Headsp 25°C / Headsp 50°C)	Determination of the amount of carbon dioxide released during incubation of material inoculated with a mixed population of microorganisms in a sealed vessel in a mineral salt medium at 25/50°C for 48 days	ASTM D5988-96 OECD 301 A
5.	Sturm test	Determination of carbon dioxide released during the degradation of material in a liquid medium (up to 6 months)	ISO 9439 ISO 14852 DIN EN 29439 ASTM D 5209 OECD 301 B
6.	Determination of carbon dioxide released (aerobic test in compost)	Determination of carbon dioxide released during the degradation of material in compost based on the organic fraction of municipal solid waste (6 months)	ISO 14855 ASTM D 6400
7.	Determination of oxygen absorbed (aerobic test in compost)	Determination of oxygen absorbed during the degradation of material in compost based on the organic fraction of municipal solid waste or activated sludge (6 months)	ISO 14851 ASTM D 5271 OECD 301 C GB/T 19276.1 JIS K 6950
8.	Anaerobic test	Determination of methane released and the degree of decomposition during anaerobic degradation of material in the presence of municipal wastewater or in compost based on the organic fraction of solid municipal waste (15, 30, 60 days)	ISO 14853 ISO 15985 ASTM D5210
9.	Determination of the degree of decomposition in compost	Determination of the degree of decomposition (mass loss) of material at elevated temperatures in model laboratory or industrial compost (3 months)	ISO 16929 ISO 20200 BS EN 14045
10.	Soil test	Determination of oxygen absorbed or carbon dioxide released during the degradation of material in natural topsoil of fields and/or forests (6 months)	ISO 17556 DIN 53739 GOST 9.060-75 (synthetic fabrics)

To infect polymer materials with microorganisms, they are inoculated with pure or mixed cultures of fungi and bacteria, as well as media with high microbial contamination (compost). As a rule, such tests are carried out under certain conditions (temperature, humidity, pH, etc.), which results in higher kinetics of biodegradation of materials compared to field tests. In addition, the biodegradability of polymer materials can be studied under conditions close to real ones, for example, in soil, fresh water, or sea water. The main disadvantage of such tests is their low reproducibility, especially in the case of field tests in environmental conditions. Complex and uncertain environmental conditions make it difficult to assess the contribution of each factor to the process of biodegradation of materials. As a rule, soil tests are carried out in conjunction with experiments in model environments.

Along with assessing the biodegradation of materials under the influence of biological factors, the ability of materials to degrade under the influence of aggressive environments, elevated temperatures (thermal degradation), UV irradiation (photodegradation), etc. is also being studied. Accelerated methods of thermal and photo-oxidation simulate the process of oxidative destruction of materials that occurs in the environment over several years. Various indicators are used to monitor the degradation of polymers:

1. Loss of material mass;
2. Biomass accumulation (determination of the microbial growth rate);
3. Oxygen uptake rate and rate of carbon dioxide (aerobic degradation) or methane (anaerobic degradation) release;
4. Change in the material surface (mechanical damage);
5. Change in the mechanical and physical properties of the material;
6. Change in the chemical composition of the material.

The most commonly determined characteristic of the biodegradation process is the rate of loss of material mass. When the material is exposed to a limited number of factors (temperature, ultraviolet radiation, a specific strain of microorganisms), the rate of mass loss is quite informative. The degree of biodegradation is determined by the intensity of microbial flora development on the material. The rate of biomass accumulation (growth) is determined by visual inspection of samples with the naked eye or using a microscope. Based on the results of the visual assessment, the material is assigned a degree of biofouling according to a standardized or researcher-established scale. The mass increase can also be determined by the difference in mass between materials with and without microbial flora. For a more accurate assessment of the intensity of microorganism growth on the material, the rate of oxygen consumption and the rate of carbon dioxide (aerobic degradation) or methane (anaerobic degradation) release are measured using various methods. The most widely used method is the Sturm method, based on measuring the rate of assimilation of the test material in an aqueous solution in the presence of fungal or bacterial microflora, recorded by the kinetics of carbon dioxide release as a result of the vital activity of microorganisms. The amount of carbon dioxide released is determined by titrimetric methods. The amount of carbon dioxide released or oxygen absorbed is used to judge the degree of mineralization of the material as a result of its use by microorganisms as a food source. Microscopic fungi, which are the main biodestructors of polymer materials, can cause their mechanical degradation and subsequent fragmentation. After testing materials for biodegradability, the surface of the material can be examined for cracks, erosion, and other mechanical damage. Biodegradation of materials leads to changes in their deformation and strength properties (tensile and impact strength, stiffness, hardness), electrical properties (dielectric strength, insulation resistance), and optical properties, so resistance to biodegradation is assessed by varying these characteristics. When studying biodegradation processes, changes in the phase morphology of the polymer matrix (degree of crystallinity, mobility in amorphous regions, etc.), surface hydrophilicity, and other characteristics are also monitored. Usually, the mechanical properties of polymer materials are determined by the length of their macromolecular chains. A decrease in the molecular weight of a polymer affects its strength characteristics. A decrease in strength can also be associated with damage to the polymer matrix or filler by destructive fungi.

Based on the above, the main goal of innovative developments in the field of biodegradable polymer materials is to select components, technological parameters, and equipment that can be used to manufacture biodegradable polymer materials that combine the required rheological, operational, and physicochemical properties with the ability to regulate the biological degradation time of finished products, minimizing harm to the environment and human health.

Since, in general, the formation of structurally ordered composite polymer systems comprising components of different nature largely depends on the conditions of their production, studying the basic patterns of formation of the above-mentioned compositions is a necessary condition for conducting an objective and reliable analysis of their properties.

2. MATERIALS AND METHODS

2.1 Materials

The following components were used to produce thermoplastic compounds: corn starch produced by Krahmaloprodukt LLC in Orel (Russia) in accordance with GOST 32159-2013; pea starch produced in

accordance with GOST 7698-93 (Russia); rice starch produced in accordance with GOST R 51953 (Russia), glycerin grade PK-94 produced by TC Vympel (Russia) in accordance with GOST 6824-96. Monoglyceride (MGD) produced by RusChimTrade LLC (Russia) in accordance with technical specifications TU 10-1197-95, sorbitol produced in accordance with GOST 32857-2014.

2.2 Research methods

Native starch of various origins: corn, rice, and pea starch was blended with glycerin and monoglyceride, varying the ratios of the components in the blend compositions given in Table 2. A plasticizing system based on glycerin/sorbitol was prepared in a similar manner.

Table 2. Composition of thermoplastic compounds

No.	wt%		
	Starch corn/pea/rice	Glycerol	Monoglyceride/ sorbitol
1.	67	30	3
2.	65	30	5
3.	63	30	7
4.	60	30	10
5.	55	30	15
6.	50	30	20

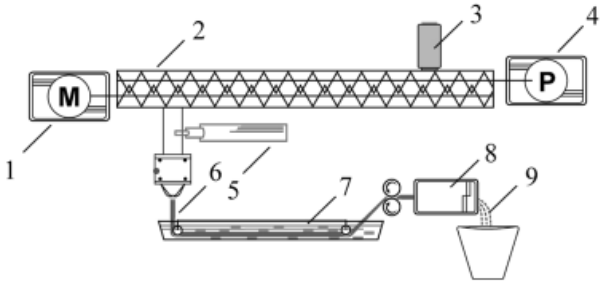


Figure 1. Installation diagram for producing thermoplastic compound granules: 1 – engine, 2 – twin-screw extruder, 3 – feed hopper, 4 – gearbox synchronized with the engine, 5 – pressure sensor, 6 – strand, 7 – cooling bath, 8 – granulator, 9 – composite granules

Native starch, glycerin, and monoglyceride plasticizer were blended for 20–30 minutes in a disperser at a rotation speed of 30 rpm. The mixture was plasticized in a laboratory twin-screw extruder with a ring die (Figure 1).

The temperature conditions for the production of thermoplastic compounds using a new plasticizing system based on glycerin/monoglyceride in the extruder zones were as follows: T1 – 77 °C, T2 – 80 °C, T3 – 90 °C, T4 – 90 °C; when using sorbitol: T1 – 80 °C, T2 – 83 °C, T3 – 87 °C, T4 – 90 °C. The resulting round-section strings were cooled and partially granulated, yielding granules 2–4 mm in size at a granulator rotation speed of 60 rpm. Figure 2 shows an example of the appearance of a string and granules of a thermoplastic rice compound.



a)

b)

Figure 2. Appearance of thermoplastic rice compound string (a) and granulate based on it (b)

The structural and morphological properties of native starches and thermoplastic compounds based on them were studied using a high-resolution autoemission scanning electron microscope JSM-7500F (JEOL, Japan).

The physical and mechanical properties of thermoplastic compound strands were determined using a Z010 ZwickRoell tensile testing machine (Germany) equipped with a computer interface with StretchTest software. The tensile strength (σp) of thermoplastic compounds was measured at a temperature of 23±2 °C and a relative humidity of 50±5% using the method described in ISO 527-3:2018 “Plastics. Determination of mechanical properties by tensile testing.” The

permissible measurement error limit did not exceed ±1%. The maximum deviations in strand diameter did not exceed ±0.2 mm. The average tensile strength was determined from 10 measurements. The tests were performed at a sample deformation rate of 20 mm/min.
The thermophysical properties were determined by differential scanning calorimetry (DSC) on a DSC 204 F1 NETZSCH (Germany) in the temperature range from 20 to 180 °C for native starches and from 20 to 140 °C for thermoplastic compounds at a scanning rate of 10 °C/min and a sample weight of 11±1 mg, in a stream of inert argon gas. The melting temperature (Tm) and melting enthalpy (ΔH) were determined from the endothermic melting peak on the DSC thermograms in accordance with GOST 55134-2012 "Plastics. Differential scanning calorimetry (DSC). General principles."

The supramolecular structure of native starches and thermoplastic compounds was studied by X-ray structural analysis. Diffraction curves were recorded on an HZG 4A X-ray diffractometer (Carl Zeiss, Jena, Germany) using copper (CuKα) radiation filtered with nickel. All curves were recorded under absolutely identical conditions, in step mode of discrete scanning. Step mode scanning, unlike continuous scanning, provides high informativeness and accuracy of the X-ray phase analysis method: the ability to precisely determine the position of diffraction reflections. The X-ray patterns of the samples under study were recorded in the "reflection" mode. The degree of crystallinity was calculated based on the intensity ratio:

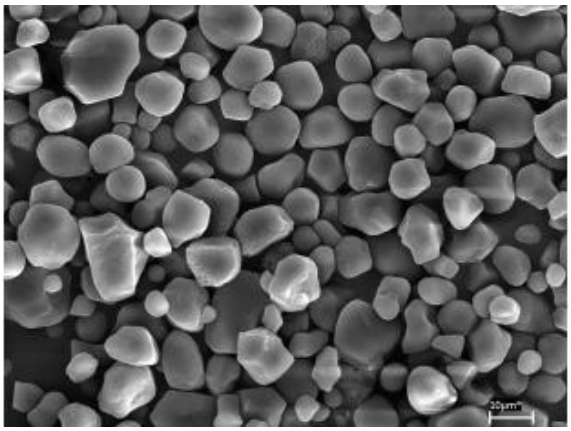
$$I_c / I_t, . \quad (1)$$

where I_c is the intensity of X-ray diffraction on crystalline areas; I_t is the total intensity of X-ray diffraction.

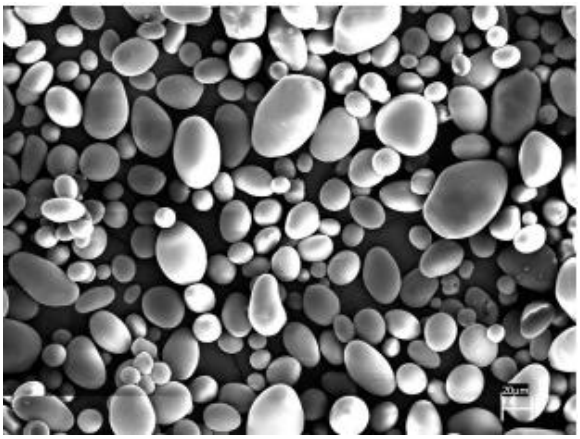
3. RESULTS AND DISCUSSION

One of the parameters when selecting native starch for the production of thermoplastic compounds and polymer compositions for use in blends with synthetic thermoplastics is particle size distribution. Using scanning electron microscopy, the morphology and size of the starch grains were determined.

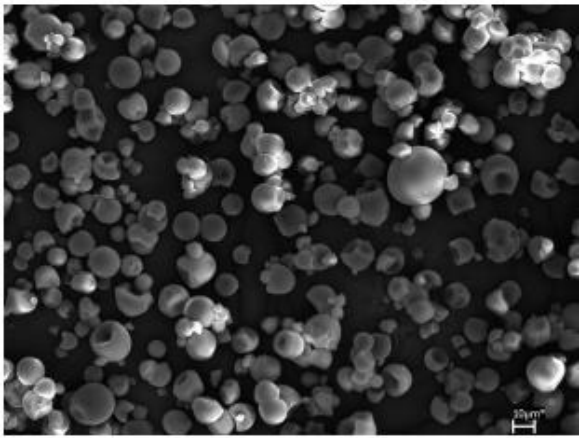
As can be seen from SEM-images (Figure 3), the morphology of starch grains varies: for example, corn and rice starch grains are characterized by a multifaceted, irregular shape, while pea starch grains have an elongated oval shape. The average size of corn starch grains varies in the range of 10.8 ± 0.4 μm, for pea starch the average size is 15.6 ± 1.6 μm, and for rice starch it is 5.3 ± 0.3 μm. Fractionation of native starches by size allows predicting their specific surface area in mixtures with glycerol/monoglyceride, as well as with glycerol/sorbitol, and influences the production of thermoplastic compounds based on them.



a)



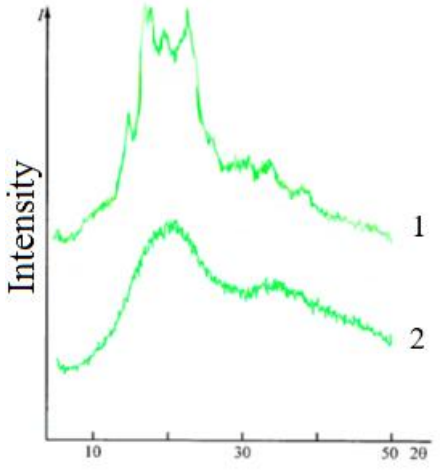
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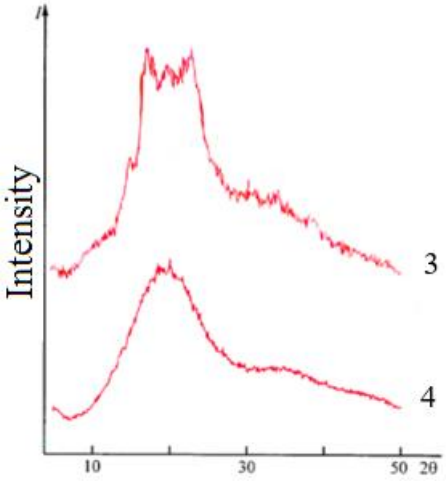
c)

Figure 3. SEM-images of starch grain morphology: a) corn, b) pea, c) – rice

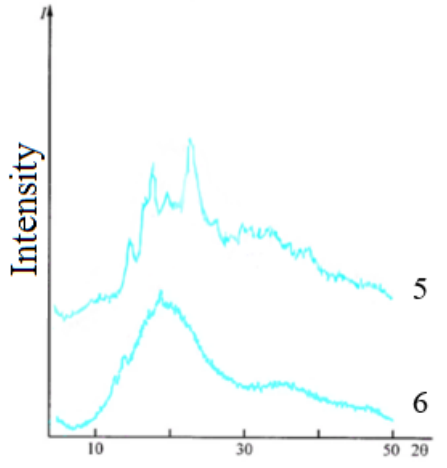
To determine the feasibility of converting native starches into a thermoplastic state, their supramolecular structure was determined using X-ray structural analysis, as well as their thermophysical properties. Figure 4 shows the diffractograms of native starches and thermoplastic compounds based on them.



a)



b)



c)

Figure 4. Diffractograms: a) native (1) and thermoplastic corn compound (2), b) native (3) and thermoplastic pea compound (4), c) native (5) and thermoplastic rice compound (6)

Native starch is characterized by an amorphous-crystalline structure with varying ratios of ordered and disordered amylose and amylopectin crystallites. The amorphous phase of native starch is formed in the presence of amylopectin in its structure, while the crystalline phase is formed in the presence of amylose.
The diffractogram of native corn starch contains four maxima at diffraction angles of 2θ = 15.2, 18.0, 20.0, and 23.0 degrees. It should be noted that the intensity and resolution of the diffraction reflections are low, which indicates the small size and defectiveness of corn starch crystallites. Along with discrete scattering from crystallites, the X-ray diffraction pattern shows a large proportion of diffuse scattering from the disordered phase of starch – an amorphous halo. The degree of crystallinity of native corn starch is 20%.

The diffractogram of native pea starch is characterized by weakly expressed diffraction reflections at angles 2θ = 15.0, 17.1, 17.9, 19.8, 21.2, and 22.9 degrees. The X-ray diffraction pattern shows a large proportion of amorphous halo caused by scattering from the disordered phase of starch. The relative degree of crystallinity of pea starch is 19.8%.

The diffractogram of native rice starch also has distinct reflections at angles of 2θ = 14.9, 17.1, 17.9, 19.7, and 22.7 degrees. Native rice starch differs from other types of native starches in terms of crystallite size, as evidenced by the different peak widths, as well as the relative degree of crystallinity, which is 39.6%.

Thus, native starches of different origins have an amorphous-crystalline structure with different ratios of ordered and disordered crystallites (lamellae) of amylose and amylopectin.

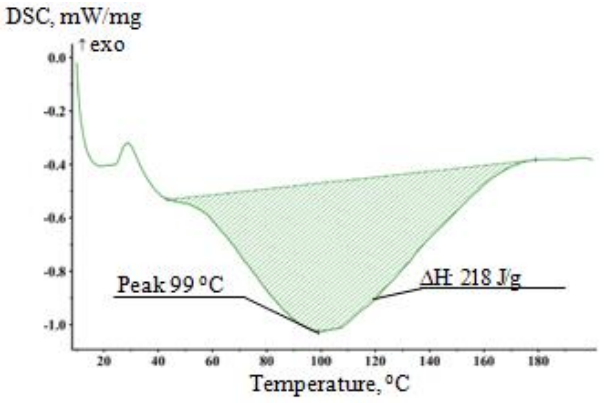
As an example, Figure 5 shows the thermophysical properties of native and thermoplastic rice compounds based on two plasticizing systems: glycerol/ monoglyceride and glycerol/sorbitol.

As can be seen from the thermograms presented, the enthalpy of fusion of native rice starch is characterized by an endothermic melting peak at a temperature of 99 °C, and the specific energy of the endothermic process is 218 J/g. For thermoplastic rice compound using a glycerol/monoglyceride plasticizing system, the endothermic melting peak is 80 °C, and the specific energy of the endothermic process is 30 times lower (7.5 J/g). For a thermoplastic rice compound using a glycerol/sorbitol plasticizing system, the specific energy of the endothermic process is 6.6 J/g. In this case, both plasticizing systems allow native starch to be converted into a thermoplastic form.

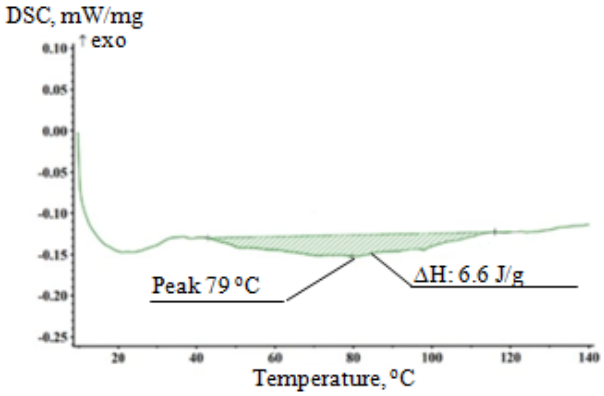
When native starch is converted into a thermoplastic form, the supramolecular structure of starch changes, as evidenced by X-ray structural analysis data: the absence of clear diffraction reflections, signs of a crystalline

structure, and the blurred nature of the curve indicate the complete destruction of the crystallites of native starch as a result of heat treatment (extrusion).

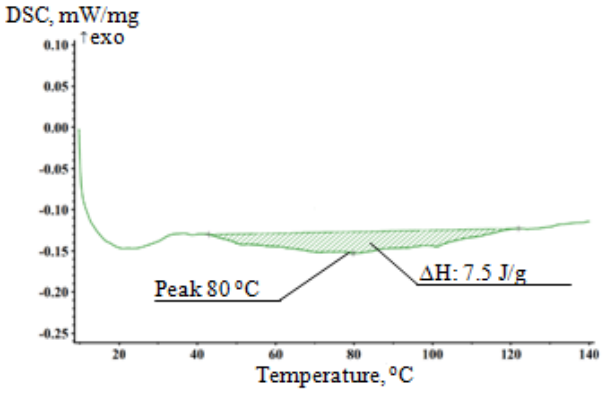
At the same time, irreversible destruction of starch grains occurs, as a result of which the macromolecules of amylose and amylopectin are released from the starch grain and partially destroyed, which is also confirmed by the determination of the thermophysical properties of thermoplastic compounds, characterized by a specific energy thirty times lower than that of native starches.



a)

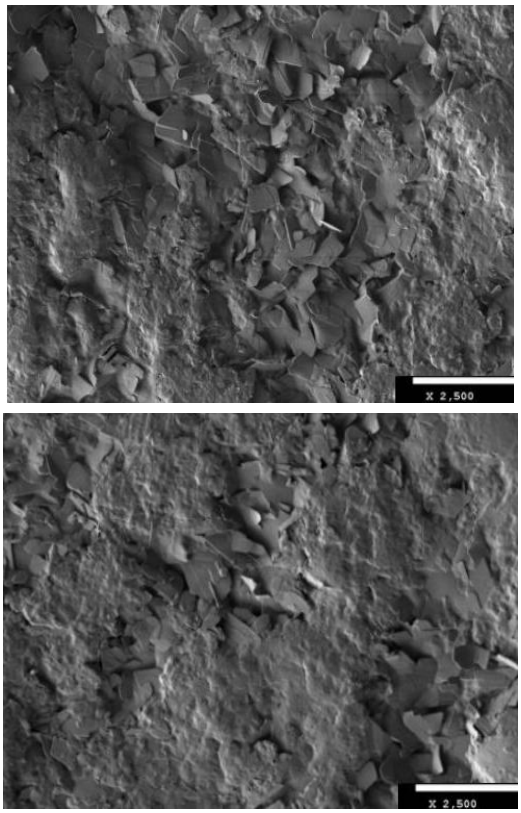


b)

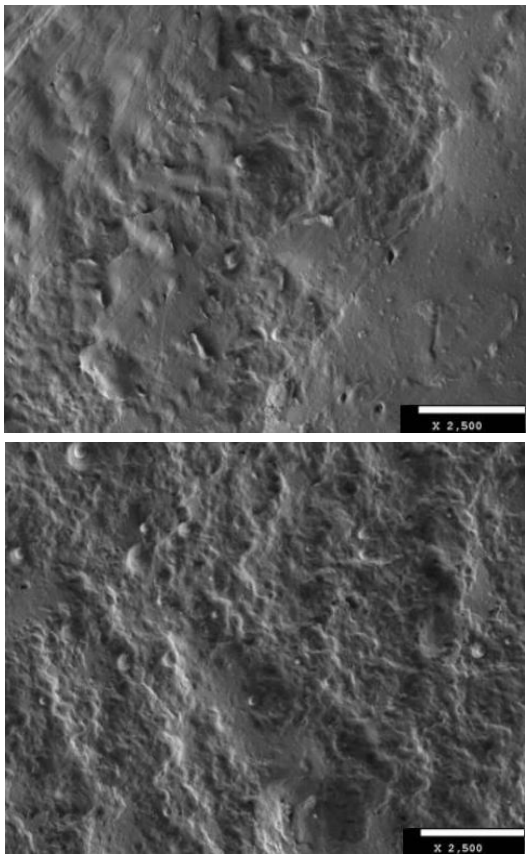


c)

Figure 5. Thermophysical properties: a) native rice starch, thermoplastic rice compound with plasticizing system: b) glycerol/monoglyceride, c) glycerol/sorbitol)



a)



b)

Figure 6. SEM images of the structural and morphological properties of thermoplastic compounds: a) sorbitol, b) monoglyceride

Thus, heat treatment causes a fundamental structural modification of native starches—their decrystallization, which affects the technological process of obtaining thermoplastic compounds—homogeneous composite melts. The smaller the size of the starch grains, the lower their melting enthalpy. This means that when the components are mixed during extrusion, such compositions will be less destructive (retain their original properties for longer), which has a positive effect on the quality of the compositions obtained. This process proves the feasibility of converting native starch into a thermoplastic state using glycerol and monoglyceride as binding plasticizers.

Considering the promising prospects of using the new glycerol/monoglyceride plasticizing system instead of the traditionally used glycerol/sorbitol, the structure of thermoplastic compounds was determined.

When producing thermoplastic compounds using sorbitol and monoglyceride as plasticizers, a heterogeneous structure is formed during extrusion in both cases. When sorbitol is used, analysis of images obtained by scanning electron microscopy shows that a structure with a clear phase boundary between starch and sorbitol is formed in the thermoplastic compound system. Such strings are characterized by visible defects. When using monoglyceride, a more homogeneous distribution in the thermoplastic compound and greater interaction with starch were observed, which manifests itself in the form of a monolithic structure visible in SEM-images. Thus, the mixture composition of a thermoplastic compound based on starch, glycerin, and monoglyceride in the extrusion process allows obtaining a homogeneous composition with a minimum number of defects.

To determine the effectiveness of the new plasticizing system based on glycerin/monoglyceride, instead of glycerin/sorbitol, the strength properties of thermoplastic starch strands based on them were determined.

As can be seen from the data presented, thermoplastic compounds obtained using a new plasticizer—monoglyceride—demonstrate a tensile strength that is twice as high as those containing sorbitol.

The optimal concentration of components at which a thermoplastic rice compound filled with monoglyceride plasticizer demonstrates the desired strength properties is starch/glycerin/monoglyceride = 60/30/10 wt%, characterized by a tensile strength of 3.3 MPa. When the starch concentration was reduced and the monoglyceride concentration in the mixture with glycerin was increased, no change in strength properties was observed in the thermoplastic compound. The thermoplastic compound obtained at the same concentration of components, but with sorbitol, is characterized by a tensile stress at break of 1.6 MPa.

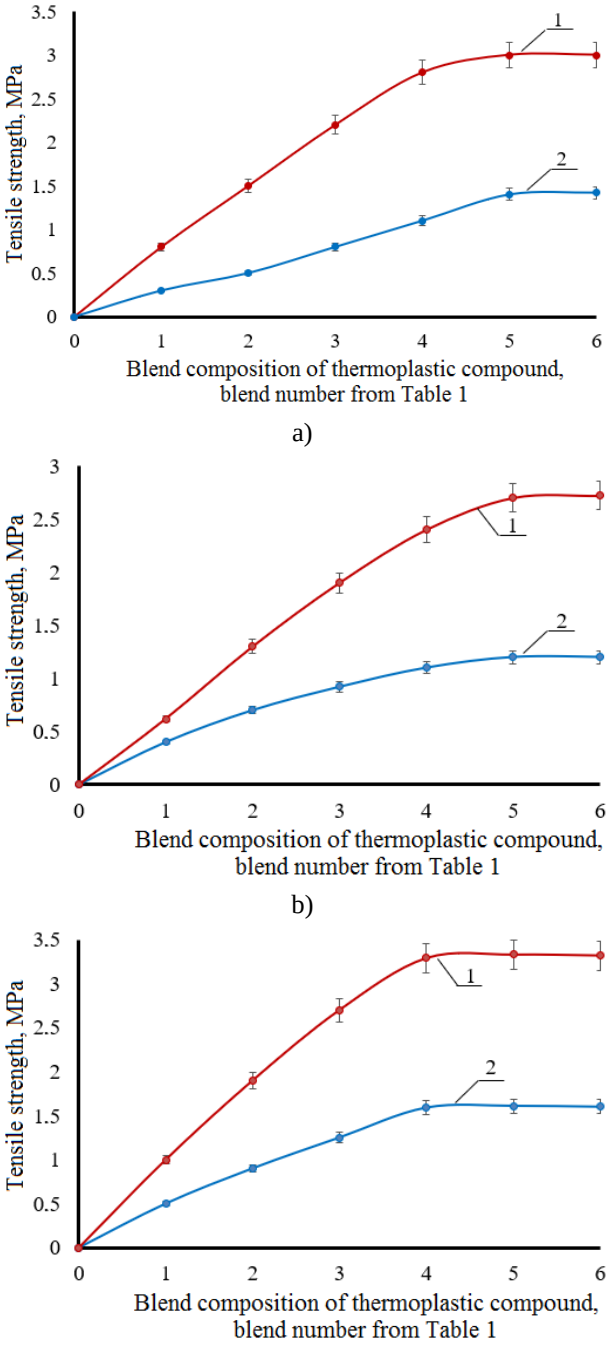


Figure 7. Thermophysical properties: a) native rice starch, thermoplastic rice compound with plasticizing system: b) glycerol/monoglyceride, c) glycerol/sorbitol)

For the thermoplastic pea compound, the optimal concentration of starch/glycerol/monoglyceride components is 55/30/15 wt%, as is the case for the thermoplastic corn compound. At the same time, the thermoplastic pea compound filled with monoglyceride has a tensile strength of 2.7 MPa, and 1.2 MPa when sorbitol is used. For the thermoplastic corn compound filled with monoglyceride, the tensile strength is 3.0 MPa, and when sorbitol is used, it is 1.4 MPa.

Thus, the promising application of a new glycerol/monoglyceride plasticizing system instead of the commonly used glycerol/sorbitol in mixtures with corn, pea, and rice starches for the production of biodegradable polymer materials has been demonstrated and proven.

4. CONCLUSION

Research has been conducted to develop a new plasticizing system based on glycerin/monoglyceride to replace the traditionally used glycerin/sorbitol for producing thermoplastic compounds based on starches of various origins: corn, pea, and rice, for use as biodegradable polymer materials.

The recipe and technological parameters for converting native starch into a thermoplastic state using a new plasticizing system based on glycerin/monoglyceride in the extrusion process have been established: the starch/glycerin/monoglyceride ratio for corn and pea starches is 55/30/15 wt% and for rice starch – 60/30/10 wt%; temperature by extruder zones: T1 – 77°C, T2 – 80°C, T3 – 90°C, T4 – 90°C.

It was found that when using a monoglyceride plasticizer, a more homogeneous monolithic structure of thermoplastic starch strands is formed, in contrast to those in which sorbitol plasticizer was used, for which a more defective structure with a phase boundary between the components was observed.
It was found that the conversion of native starch to a thermoplastic state using the new plasticizing system, as in the case of sorbitol, is accompanied by a change in the phase state, resulting in the decrystallization of the original starch.

It has been established that the conversion of native starch into a thermoplastic state using a new plasticizing system, as in the case of sorbitol, is accompanied by a change in the phase state, resulting in the decrystallization of the original starch. At the same time, the mechanical properties of thermoplastic compounds using the new plasticizer, monoglyceride, are twice as high as those of thermoplastic starches produced using sorbitol.

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