THERMOPLASTIC COMPOSITION WITH MODIFIED POROUS CORN STARCH OF BIODEGRADABILITY PROPERTIES

Prof. Dr. Valentina Kolpakova[1]
PhD Student Ivan Usachev[2]
PhD Aleksandr Papakhin[3]
Sc. **Aslan Sardzhveladze**[4]
PhD Vladimir Ananiev[5]

[1, 2, 3, 4]All-Russian Research Institute for Starch Products – Branch of V.M. Gorbatov Federal Research Center for Food Systems of the RAS, Russia

[5]Winogradsky Institute of Microbiology Federal Research Centre «Fundamentals of biotechology» of the RAS, Russia

ABSTRACT

The purpose of research works was to develop a thermoplastic composition with porous (modified) corn starch used to give biodegradable properties to a synthetic polymer (polyethylene of low density) with more effectively, than native corn starch. The expected effect is a wider range of modifying components for biodegradable polymeric products based on polyethylene, reduced emissions polluting the environment due to more intensive decomposition in surrounding conditions (light, atmospheric precipitation, microorganisms etc). For this purpose, there are defined ratios of the principal component (porous starch) and softeners (sorbitol, glycerin) to improve physicomechanical properties of thermoplastic starch and the polymeric composition prepared on its basis. There are specified parameters of thermoplastic starch and polyethylene film based on the hybrid composition with porous starch received by extrusion.

Beforehand the way of enzymatic modification of native starch by its hydrolysis is developed for receiving a hybrid composition with porous corn starch at the temperature below the initial point of gelation in the presence of amylolytic enzymes. Starch had a particular degree of hydrolysis, made in the heterogeneous medium and under optimal conditions. Physicomechanical characteristics of a film at a various ratio of components are investigated with taken into account standard values of the maximum tension and the specific break extension. The composition had rheological characteristics corresponding to requirements claimed to materials being processed on the traditional equipment for plastic. Film products had the production characteristics indicating the ability to decay in vivo with greater speed, than products with native corn starch.

Keywords: *corn starch, thermoplastic composition, extrusion method, polymeric film, biodegradability*

INTRODUCTION

Due to the increase in production of polymeric products great attention is given to the problems of environmental pollution and rational use of natural resources therefore issues of processing of the used polyethylene products are sharp and relevant [1], [2] today. In the world about 130 million t of plasts from natural raw materials, including from hydrocarbons are produced. However, the volume of biodegradable materials is only about 7-8 thousand tons per year. According to experts forecasts, by 2020 production of biodegradable products will reach 1.3 million t. At the same time, there was such an approach at which such products were made that kept operational properties only during the period of consumption and operation, then it is exposed to the destructive transformations under the influence of environmental factors [3], [4]. Destruction products easily join in metabolism processes of natural biosystems, at the same time they decay to various gases, waters, etc. For the creation of such products, the perspective direction is to develop composition polymeric materials with properties of biodegradability.

Among the variety of natural polymers starch is of keen interest for such compositions from [5], [6]. Starch isn't the true thermoplastic, but in the presence of softeners (glycerol, sorbitol etc.) at high temperature (90–180 °C) and shifts it melts, becomes diluted to be used on the molding, extrusive, inflate equipment for synthetic plastic. When receiving thermoplastic starch (TPS) besides glycerin, sorbitol it is used xylitol, maltit, propylene dicarboxylic acid, etc. up to 33% to the mass of starch. Physicomechanical properties of the plasticized starch significantly depend on the type and molecular weight of the softener: its molecular weight increases as glass transition and durability of the material linearly grow, but moisture absorption and the specific break elongation decrease. The type and amount of the softener play a defining role in the formation of strength properties of the material. Therefore, change of glycerol amount from 15 to 35% in compositions leads to a decrease in glass transition, tensile strength and to increase in the specific elongation.

We also developed TPS technologies in which optimum compositions are made by means of mathematical scheduling with the use of low-density polyethylene and native (unmodified) starch [7], [8]. Starch is a natural polysaccharide, which is contained in plants and fruits. The structure and properties of starch easily are modified with different types of influences with receiving a wide range of sugary products. Enzymatic reactions of complete or partial hydrolysis are one of the ways to change properties of starch. The modern ways of starch conversion include stages of a gelation and a dilution of its 15-35% suspensions by heating to 95-120ºC with a thermostable alpha amylase and the subsequent saccharification of the diluted product with a glucoamylase or a glucoamylase together with pullulanaze at 60±5ºC. This way demands high energy consumption that causes the high prime cost of the received products. In recent years the interest in studying of effect of enzymes on native (nongelation) starch to expand of the sugary products range with given carbohydrate structure and properties increased in the world. In the All-Russian Research Institute of Starch Products research works were made on studying the effect of amylolytic enzymes on native starch of various origin and it was developed a new technology without pregelatinization at particular concentrations of the suspension [9], [10]. Unlike the traditional scheme the technology allows to receive two products during one technological process: modified porous starch having properties other than those of native starch, and glucose syrup of high quality.

The purpose of this work is to develop TPS using modified porous corn starch capable to give higher biodegradable properties to synthetic hybrid polyethylene compositions, in comparison with native starch.

MATERIALS AND METHODS

Corn starch (GOST 32159-2013) was used as the raw material. Indexes of starch quality were determined by the GOST 7698-93 methods "Starch. Acceptance rules and methods of the analysis". Amylolytic enzyme preparation of a glucoamylase OptidexL 400 of *Asp. niger* is provided by the DuPont™ Danisco company (USA). The Glyucoamylase activity of the preparation OptidexL-400 was defined in accordance with GOST by P 54330-2011. The quantity and carbohydrate composition of soluble dry solids of starch were determined with solution chromatography on the analyzer of carbohydrates of Bischoff 8120 (Germany) and a refractometer of the ATR brand of Schmidt (Germany). The mass fraction of the reducing substances (a glucose equivalent) was determined by Lane-Eynon's (GOST 52060-2003) method. Viscometric properties of starch were investigated on the RVA-TecMaster express analyzer, thermodynamic properties were determined on a micro calorimeter DASM-4 (Russia). The form and the grains type of the native and enzyme modified starch were defined on a light microscope of DMLM (Leica, Germany). The adsorption capacity (ADC) of starch was determined by a spectraphotometric method with a food dye of E122. Definition of chemical composition of raw materials and end products, pH values of the medium, dry solids was made by the techniques accepted in starch syrup production.

For the preparation of TPS there was used: distilled glycerin PK-94 (GOST 6824-96); sorbitol with indexes of quality by the Certificate of conformity and low-density polyethylene (PELD) 11503-070. All raw materials and by-products met the requirements of TR CU 021/2011. All raw materials and by-products conformed to the requirements of TR CU 021/2011. Biohybrid composition (BHC) was made of PELD and TPS on a laboratory extruder at a ratio of components 70:30 of PELD and TPS. The extrusion temperature for TPS was 115 °C, for BHC 150 °C. Breaking stress at stretching and the specific break elongation of BHC and composition films were measured at 23±2 °C and 50±5 % relative humidity by the method explained in GOST 14236-81. To test plaits of BHC and composition films there were cut out strips of 10 mm wide, marks were put to limit the plait length, equal 50 mm and a 2-3 mm diameter. The experiment was made on a break tension testing machine of RM-50 brand equipped with the computer interface. The limit of the allowed value of a bias of loading didn't exceed ± 1 %. The maximum deviations of a diameter of a sample made ±0.2 mm. Manufacture of film samples from polyethylene – starch compositions was carried out by method of flat slit extrusion also on a laboratory unit with an extruder with a diameter of 12 mm. The film was accepted on a metal shaft of a receiving device, it was investigated the slide of films which wasn't contacting to the cooling shaft. A melt flow index of compositions (MFC) at 190

°C was defined in accordance with GOST 11645-72, microbiological stability of films was defined according to GOST 9.053-75 and GOST 9.049-91. All chemical reagents were chemically pure.

RESULTS AND DISCUSSION

At the first stage there were received samples of porous corn starch according to our flow diagram [9], [10] and stages:

- dilution of starch in distilled water to receive suspension with the given concentration of the dry solids (DS), finishing pH of suspensions to a desired value;

- heating of suspension in a shaker incubator IKAKS 4000i (Germany) up to 50-52 °C, feeding an enzyme preparation, keeping of a reaction mixture within 12-72 h at a temperature of 52±0.5 °C and continuous mixing with periodic sample drawing;

- filtering of a reaction mixture under vacuum with receiving a filtrate and a deposit of not hydrolyzed starch; washing of a deposit;

- mixing of a filtrate with washing waters, cooking them up to DS 72-74 % and receiving glucose crystals;

- drying of a deposit (the modified porous starch) at 45-50 ºC with the subsequent refinement on a laboratory mill.

At the second stage with the use of porous starch, it was developed a new extrusive composition of TPS for biodegradable packing products using the same softeners, as with native corn starch: that is glycerin and sorbitol [8]. The ratio of components for TPS was defined, as well as for native starch, by drawing up a mathematical matrix of the experiment scheduling and soling the corresponding equations with use of results of experiments on a laboratory extruder. For this purpose, it was chosen the orthogonal central composition plan of the second order with "star brachiums" allowing to get on the basis of the results 15 tests rather reliable mathematical model as the complete simple equation of the 2nd order with three factors which were describing the corresponding response of a system. Coefficients were searched for the following equation:

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+B_{12}X_1X_2+B_{13}X_1X_3+B_{23}X_2X_3+b_{11}X_1^2+b_{22}X_2^2+b_{33}X_3^2$$

As factors there are chosen the following parameters:

X_1 – extrusion temperature; X_2 – starch content in the composition; X_3 – a screw rotation frequency.

As responses there were physicomechanical characteristics of compositions, that is breaking stress at stretching (σ) and the specific break elongation (ε). The experiment matrix with variation levels of the factors and their actual values is made. The algorithm of calculation of coefficients of the regression equations describing mathematical models of response functions is developed. Coefficients are calculated in Microsoft Office application of Excel. The received 15 samples of compositions are based on polyethylene and corn starch, strength and deformation indexes of samples are defined, coefficients of the equations of system responses are calculated. The test data calculated with the developed algorithm in Microsoft Office application of Excel of the response equation (1) and (2) are given below:

$$\sigma=5,5+0,165X_1-0,537X_2-1,322X_3-0,459X_1X_2+2,52X_1X_3+1,178X_2X_3+0,546X_1^2+0,786X_2^2+0,205X_3^2. \quad (1)$$

$$\varepsilon=40-4,132X_1+4,132X_2-4,132X_3+49,746X_1X_2+32,01X_1X_3+37,114X_2X_3-3,415b_{11}X_1^2+3,415X_2^2-10,216X_3^2 \quad (2)$$

It is established that the best rheological characteristics of TPS (the ultimate strain at stretching – not less than 4 MPa and the specific break elongation - not less than 15 %) were received at a ratio starch: glycerin: sorbitol - 60:30:10, at 115 °C on the extruder exit and at 60-80 r.p.m. of the screw, as well as for native starch.

Further on the basis of PELD with the addition of TPS prepared on the basis of porous modified starch in an extruder it was prepared biohybrid composition (BHC) with polyethylene at a ratio 35÷30 - 65÷70 and the temperature of 140 °C [8]. From the received BHC granules on an extruder with an orifice slit there was received a composite film 100÷410 microns thick of the following structure: PELD - 65-70 %, poros starch - 18-24 %, glycerin of 9-12 %, sorbitol 3-4, in % on total composition volume.

The choice of optimum ratios of the polymer and TPS was caused by a limit, which was defined by interaction force on a demarcation of starch hydrophilic and polyethylene hydrophobic phases. BHC composition was used as a control sample for a research of properties that was prepared with TPS from native corn starch at the same ratio of components. The control composition had insufficiently high operational properties such as low water absorbing capacity (table 1) which value is important for the course of processes of biodegradability.

Table 1. Biochemical, physicochemical characteristics of native and porous corn starch

Type of starch	Degree of hydrolysis, %	WCA, g/g	WS, g/g	Dynamic viscosity, MPa·c	Enzyme attack, % on DS
Native starch	0	1.16±0.05	0.31±0.03	38.2±1.30	46.4±0.06
Porous starch	52.2±1.2	1.78±0.03	1.28±0.20	23.0±0.09	52.0±0.07

Note: WCA is the water connecting ability; WS – water solubility

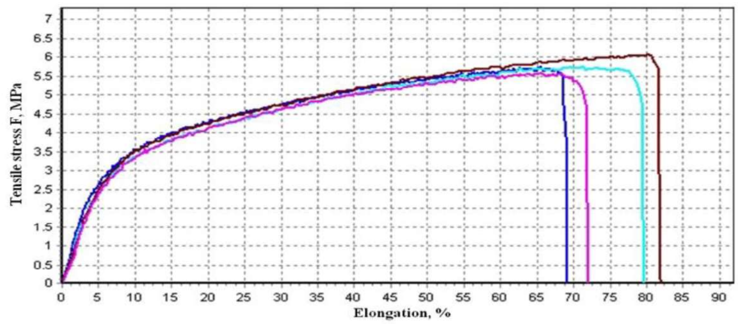
Thanks to enzymatic hydrolysis in the course of a biocatalysis numerous radial cavities and pores of various depth were formed on the surface of grain of starch due to that modified porous starch, in comparison with the native one, had a larger surface pore area, lower molecular mass due to reduction of the length of polysaccharide chains of amylose and amylopectin. It had the increased adsorptive, water connecting (by 1.6 times) ability, solubility – by 4 times and by 1.6 times smaller dynamic viscosity (table 1).

The increased degree of hydrolysis of the modified starch (52.2 %) and increase by 24 % of its enzyme attack with amylases, in comparison with native starch, are very important for reduction of biodegradation time of polymeric films. The advantage of corn starch before native one was more extensive surface of pores thanks to what the surface and the area of interaction of starch with softeners and polyethylene increased that provided more uniform distribution of components on all surface of the thermoplastic composition and larger extent of change of properties in the course of biodegradability. The molecules of porous starch interacting with hydroxyl groups of sorbitol and glycerin, having the increased water connecting ability, solubility and an attack with enzymes, can be exposed to destructions under the influence of external factors. Products of a destruction are capable to break the structure of polyethylene with a caving, cracks into which water, microorganisms can get and other factors can also cause the accelerated decomposition.

Typical differences in the studied physicomechanical characteristics of test and control samples are shown in table 2 and in figure 1. Results showed that in an sample with porous starch the specific elongation (elastance) and tensile stress of a film increased by 60-63% that testified, on the one hand, about the opportunity to decay with greater speed in vivo if to consider the ability value to lengthening, and on the other hand, about the increase in product resistance in use.

Table 2. Physicomechanical indexes of a film with TPS

TPS with native starch		TPS with porous starch	
tensile stress, MPa	specific elongation, %	tensile stress, MPa	specific elongation, %
5.92±0.17	69.74±6.90	7.62±1.00	146.46±6.14



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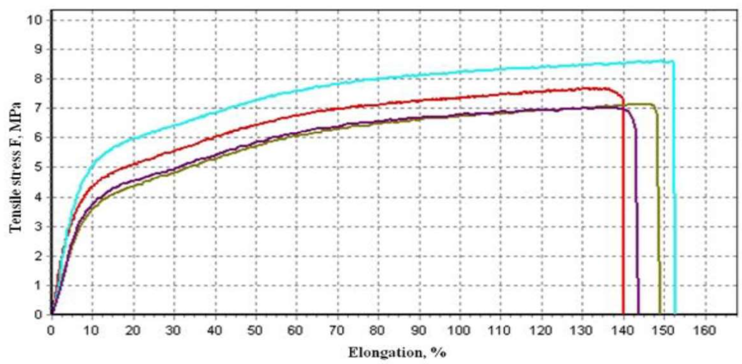

B

Figure 1. Graphs of tension from lengthening of a film with TPS from native (A) and porous starch (B)

Changes of physicomechanical characteristics of the films prepared by the options given in table 3 within 6 months storage in a biohumus are presented in table 4.

Table 3. Structures of polyethylene compositions with native and porous starches

№ sample	Native starch, %	Composition of TPS, %			PELD
		Porous starch	glycerin	sorbitol	
control	18	-	9.00	3.00	70.0
1	-	18.0	9.00	3.00	70.0
2	-	19.5	9.75	3.25	67.5
3	-	21.0	10.50	3.50	65.0

It is visible that values of breaking stress (durability) and tensile elongation (elastance) of test pieces compositions, in comparison with the control one in which native starch was used worsened for 20-35 % and 35-44 %, respectively. Therefore, in film test samples degradation processes of the polymeric composition proceeded more intensively, than in the control sample with TPS containing native starch.

Table 4. Physicomechanical characteristics BHC with native and porous starches

№	MYP, / 10 min	Changes, % *		Microbiological seeding of 10 cm of a surface
		specific elongation, %	tensile stress, MPa	
C	0.19±0.02	0 (102.16%)	0 (6.4 МПа)	1x30 ед. ±6
1	2.50±.,10	35.0±1.1	20.0±2.0	1x65 ед. ±7
2	2.64±0.20	38.0±2.0	24.0±1.7	1x72 ед. ±4
3	2.74±0.30	44.0±3.1	35.0±1.0	1x80 ед. ±6

*) change of deformation strength after keeping in a biohumus within 6 months, %; MYP – a melt yield point; C – a control sample

CONCLUSION

Theoretical bases and the technological modes of the low-temperature biocatalysis of native corn starch with the particular degree of hydrolysis (52.2%) are developed. Data on physical and chemical, structural and functional properties of the modified starch of a new type are obtained. It is expedient to use porous starch with this degree of hydrolysis in extrusion to manufacture thermoplastic starch with low density polyethylene for the film products capable to biodegrade. At storage in a biohumus physicomechanical properties (the maximum durability and the specific break elongation) of the products with porous starch changed more often (for 20-44%), than of the films with native corn starch. The obtained data confirmed the course of destructive processes in test samples of products.

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