Study of structure and properties of biodegradable composite films based on thermoplastic starch

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Abstract. The increasing use of plastic products is causing pollution of nature with micro plastics, plastic waste and harmful substances. In this work, the possibility of obtaining thermoplastic starch was studied; its structure and properties were investigated. The biodegradable compositions based on polyethylene-starch and polyethylene-thermoplastic starches were obtained, in which starch was used as a filler in the polyethylene matrix. Comparative studies of composites properties, such as optical, physic-mechanical, rheological and biodegradability were carried out. The polyethylene-thermoplastic starch-based composite films with biodegradable properties can be used as packaging materials instead of packaging polyethylene bags.

1 Introduction

Today, the world's production of synthetic polymers exceeds 360 million tons per year, half of which spent on the production of disposable packaging products [1]. It leads to the accumulation of plastic waste and consequent contamination that generate greenhouse gases and harmful substances. The scale of the negative impact of the plastic waste problem on the ecosystem is increasing year by year. One of the current challenges is the creation of compositions with biodegradable properties through the production of new polymers with biodegradable properties and the modification of existing synthetic polymers for industrial production. To address this issue, the UN has enacted laws regulating plastic products in 127 countries and banned the use of disposable plastic products in 27 countries [2]. There are several methods of disposing of synthetic polymer waste [3] and one of the scientifically based directions is to create compositions based on biodegradable polymer. Replacing petrochemical-based polymers with biopolymer-based renewable alternatives is becoming increasingly important at a time when nature is facing an environmental crisis [4-5]. The concept of using biodegradable polymers as a material is not new. The first patents for biodegradable packaging films based on natural polymers used to extend the shelf life of food products were granted in the 1950s [6]. Starch is cheaper and more common than other natural polymers with biodegradable properties, which makes it widely available as filler for the production of biodegradable plastics [7]. However, due to low water resistance and low strength performance starch is often mixed with other polymers to achieve high

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mechanical properties. Comparative studies of physic-chemical properties and structure of cotton cellulose and its modified forms [8] with biodegradable properties are used in the composition with synthetic polymers. The mechanical optical and rheological properties of the composite films obtained on the basis of starches derived from various plants with polyethylene were studied, [9] and it was found that the properties of the composition containing the starch of powdered corn were good. Plasticizers (organic and nonorganic substances) are often used in order to provide of starch with thermoplastic properties [10-11]. The process of thermoplasticization of starch is also call gelatinization. As a plasticizer for the gelatinization process, mainly water [12], glycerin [13-14], sorbitol, sugar, ethylamine, form amide [15-16], polar molecules are used.

Thermoplastic starch (TPS) obtained by bringing the starch to thermoplastic properties under the influence of plasticizers by high temperature and pressing in extrusion devices for synthetic polymers [17]. There are some parameters of the extrusion process such as screw speed, sample moisture content, process temperature, extruder pressure, etc. which have important influence on the properties of TPS [18-20]. The aim of the work is to provide starch with thermoplastic properties and to obtain polyethylene / starch compositions and investigate their properties.

2 Materials and methods

Materials for the study were F-0320 low-density linear polyethylene (PE), produced at the "ShurtanGas Chemical Complex", corn starch (St) for food produced by Russia's "AMILKO" LLC, glycerin and sorbitol as plasticizers. The molecular structure of the plasticizer plays a crucial role in shaping the hydrogen bonding system and the strength properties of the material. Studies have described the mechanisms by which a starch molecule forms hydrogen bonds with glycerin and sorbitol.

The starch was dried at 80°C for 12 h and the gelatinization process under the action of plasticizers was carried out in a single screw laboratory extruder (speed 50 rpm) at 105-115-125°C (Table 1).

Table 1. The amount of plasticizers in the gelatinization process

Sample code	The amount of plasticizer (%)	Plasticizer (glycerin: sorbitol) ratio
TPS1000	10	1:0
TPS2000	20	2:0
TPS3000	30	3:0
TPS1326	39	1:2
TPS2613	39	2:1

The twin screw laboratory extruder (D = 22.5 mm; L/D = 40:1, speed 70 rpm) was used for obtaining polyethylene/TPS compositions at 155-160-165-175-180°C; ratio of PE/TPS - 80/20, 70/30. The films based on compositions were formed using laboratory single screw blower extrusion equipment (D = 25 mm; L = 20, speed 60 rpm, zone temperature – 170^0C, 180^0C, 190^0C, 180^0C).

The structure of the films examined under the "Motic MBI-6" optical microscope. The mechanical properties of the films studied in accordance with GOST-14236 on the equipment of the universal breaking machine *Shimadzu AG X-plus* (Japan). The parameters of the crystal structures of TPS samples were determined by X-ray diffractometer XRD MiniFlex 600 (Rigaku, Japan) using Cu-Ka as a radiation source. The scanning range was 2°/ min, in the range of 5–40°, with the generator rated at 22 kV and 12 mA. The structure of the samples was tested using FTIR spectrophotometer "Inventio-S" (Bruker, Germany)

in the range of 500 cm^1 to 4000 cm^1. Melt flow index (MFI) of compositions studied in accordance with GOST-11645 on the *Tester DH-MI-BP*. Density of samples tested on the electronic densmeter of "*MDJ-120S"* in accordance with GOST 15139-69.

3 Results and discussion

Comparing the IR spectra of TPS samples obtained under different conditions it observed that the amount of hydrogen bonds in the TPS sample increased with the increase for plasticizer used in the gelatinization process due to the peak intensity formed in the 3400cm^{-1} area belonging to intermolecular hydrogen bonds during starch gelatinization.

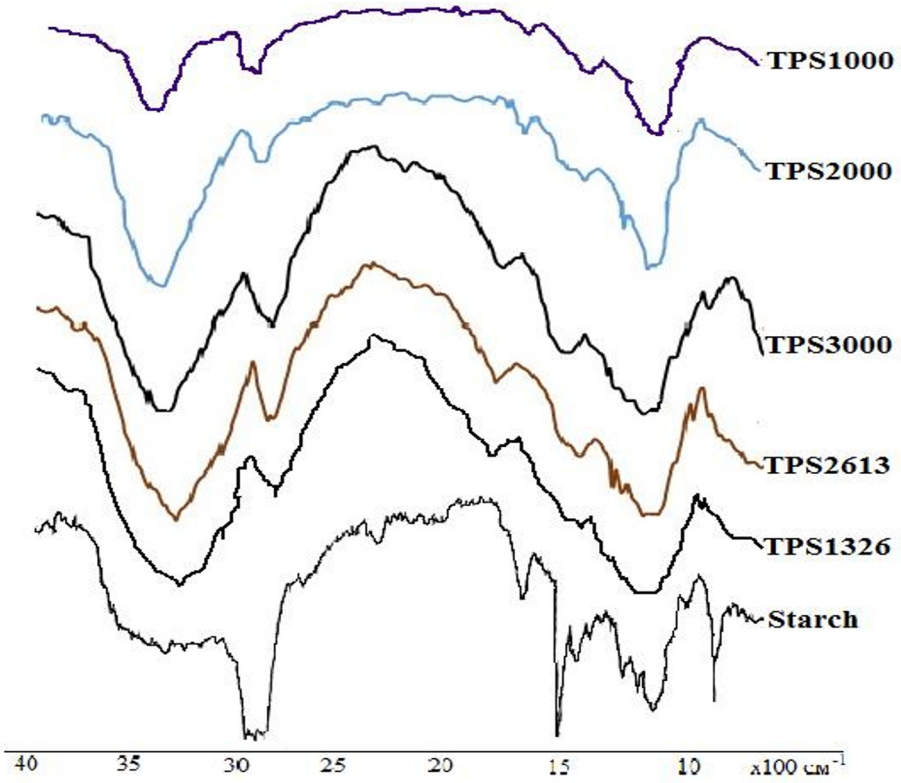


Fig. 1. IR spectrum of TPS samples

Diffractograms of crystal structures of TPS are shown in Fig. 1. Because of gelatinization of starch, its crystal structure parameters changed, the degree of crystallization decreased and the formation of new crystals of type V_a-type at 18.3° and V_h-type at 20.3°, which are not presented in natural starch [21].

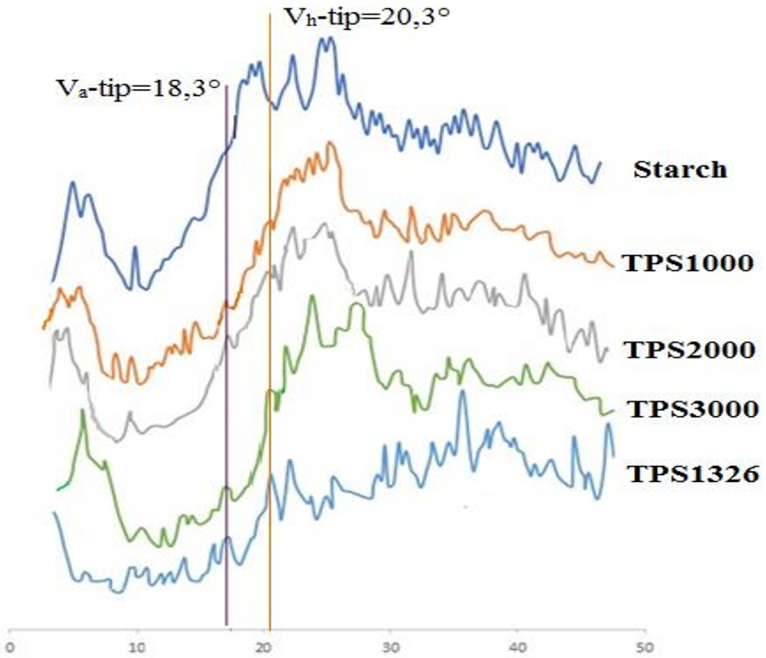


Fig. 2. X-ray diffractograms of TPS samples

As the amount of plasticizer used in the TPS increased, the intensity of the peaks showing crystals increased.

The density and melt flow index (MFI) of compositions were determined (Table 2).

Table 2. Density and MFI of PE compositions

Sample code	The amount of filler	Filler type	Density	MFI (g/10min)
PE	0	-	0.92	3.10
PE80St20	20	Starch	0.95	2.52
PE70St30	30	Starch	0.99	2.10
PE80TPS(3000)20	20	TPS1326	0.97	2.60
PE70TPS(3000)30	30	TPS1326	1.02	2.22
PE80TPS(1326)20	20	TPS3000	0.98	2.65
PE70TPS(1326)30	30	TPS3000	1.08	2.35

The particles and partially agglomerated particles of starch are observed in PE/St composite films, while in the PE/TPS films TPS is evenly distributed in the PE matrix. (Fig. 3)

a *b* *c*

Fig. 3. Optical microphotograps of PE70/St30 (a), PE70/TPS(3000)30 (b) and PE70/TPS(1326)30 (c) composite films

The mechanical (tensile strength, relative elongation) and optical (light transmittance) properties of composite films depend on quantity of fillers, that is to increase of amount of fillers to decrease these properties. The mechanical and optical properties depend not only on the amount of filler but also on the type of filler used.

Table 3. Physical-mechanical and light transmittance of films based on PE compositions based on Kr and TPS

Sample code	Tensile strength, (MPa)	Elongation at break, (%)	Light transmittance, (%)
PE80St20	6.6	106	88
PE70St30	5.5	85	84
PE80TPS(3000)20	14.1	448	91
PE70TPS(3000)30	12.5	430	87
PE80TPS(1326)20	15.2	460	93
PE70TPS(1326)30	13.8	443	89
PE	17	600	99

The biodegradability of composite films was studied. There are a number of specific standardized methods for determining the biodegradability of plastic products, each of which based on changes in various parameters, carried out under special conditions. In this case, the mass of the films was determined by monthly inspection by burying in bio humus enriched with specially prepared putrefactive microorganisms to determine the biodegradability of the films in an accelerated state.

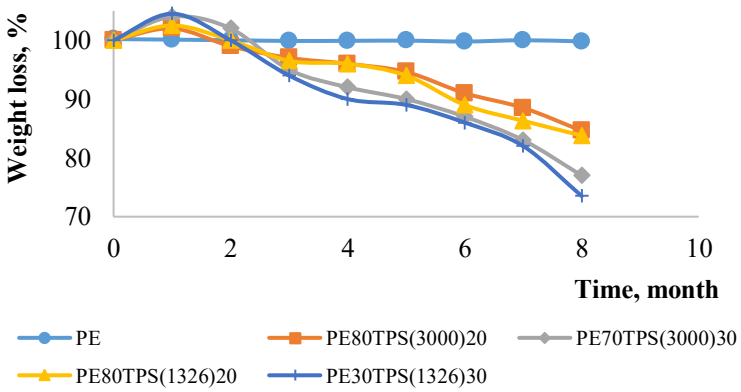


Fig. 4. Mass changes of PE and PE / TPS composite film samples embedded in bio humus over time

The results show the weight of PE/TPS composite films was decreased over time. It can be explained by the biodegradation of the filler in the composition. It was found that film weight is decreased with increasing amount of TPS in composition. It was found the mass change of the sample using a filler containing TPS (1326) higher than TPS (3000). The weight change of the composition PE70/TPS (1326) 30 was up to 26.5% during 8 months.

The biodegradability of composite films was also studied based on changes of mechanical properties. In this method, the biodegradability described by determining the mechanical properties of the samples buried in a special medium at different intervals.

Table 4. The tensile strength (MPa) of the films stored in the initial and different period biohumus

Sample code	Before, MPa/remaining mass	After 2 month, MPa/remaining mass	After 4 month, MPa/remaining mass
PE	17 MPa 100%	16.8 MPa 99%	16.5 MPa 97%
PE80TPS(3000)20	14.1 MPa 100%	12.1 MPa 86%	9.6 MPa 68%
PE70TPS(3000)30	12.5 MPa 100%	9.4 MPa 75%	5.8 MPa 46%
PE80TPS(1326)20	15.2 MPa 100%	13.4 MPa 88%	10.6 MPa 70%
PE70TPS(1326)30	13.8 MPa 100%	10.5 MPa 76%	6.6 MPa 48%

It was observed mechanical properties become worse with increasing stored period of films in bio humus and the relative change value was greater in case of composite PE/TPS (1326) than PE/TPS (3000).

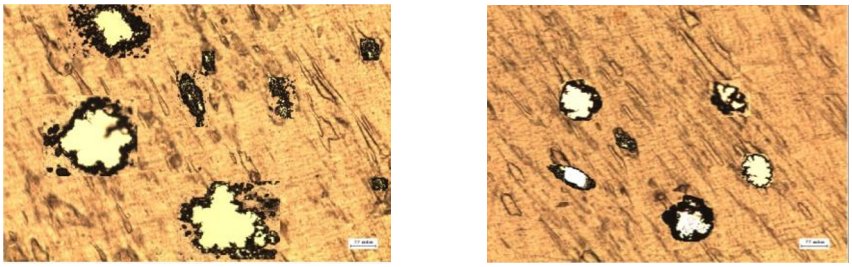
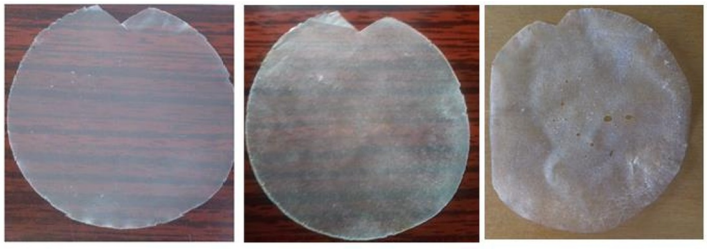


Fig. 5. Optical microphotography of PE70TPS (1326) 30 (a) and PE70TPS(3000)30 (b) stored in bio humus

Optical microphotographs show that micro-holes were appeared in the films because of the decomposition of the composite film samples stored in the biohumus.



a *b* *c*

Fig. 6. Changes of the appearance of PE70TPS (1326) 30-film stored in biohumus: a-initial b- after 2 months, c – after 6 months

The appearance of the film samples stored in the bio humus was also changed and the formation of holes was observed.

4 Conclusions

The process of gelatinization of starch with different plasticizers (glycerin and sorbitol) was studied and optimal conditions of obtaining thermoplastic starch were determined. The compositions PE/TPS with different ratio of components were obtained and investigated by IR spectrometry, X-ray methods. The biodegradable composite films based on PE/TPS were formed and biodegradability of films was investigated using standard methods. The change and deterioration of the appearance and mechanical properties of the films after storage in vermicompost over time is shown.

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