

## GLOBAL TRENDS IN BIODEGRADABLE POLYMERS

Ivan Usachev<sup>1</sup>

Dmitry Solomin<sup>2</sup>

<sup>1,2</sup> All-Russian Scientific Research Institute of Starch Products - a branch of the Federal State Budgetary Scientific Institution "Federal Scientific Center for Food Systems named after V. M. Gorbатов" RAS, Moscow, Russia

### ABSTRACT

Recently, the rapid and almost uncontrollable growth in the consumption of synthetic plastics in many sectors of the economy, especially in the field of packaging, has been a serious concern. Plastic containers are used for packaging food products, medicines, electronic devices, liquids, including those with a higher hazard class, etc. [1]. According to the German Nova-Institute, the global plastic production in 2020 has reached almost 400 Mill. Tons. At the same time, the volume of biodegradable plastics obtained from renewable resources amounted to only 3.5 million tons, i.e., about 1% of the total volume production [2]. Considering that only 25% of plastic waste is recycled, the growing consumption of polymer products is forcing manufacturers to develop biodegradable polymer compositions [3]. The problem has economic and environmental aspects since it is interconnected with the growing need to protect the environment and reduce the cost of raw materials for the production of various products.

*Keywords: biodegradable polymers, biodegradable materials*

### INTRODUCTION

It is considered promising to develop technologies for biodegradable polymer hybrid compositions (BGC) and products based on them [4], [5], [6]. One of the promising directions for the creation of BGK is the use of thermoplastic starch (TPS), as the main component for their base [7]. To obtain TPK, native starch is mixed with heating with various plasticizers [8]. It is known today that the use of TPK as a filler in polyolefin compositions instead of native starch is preferred due to better processability and higher thermal stability. In this case, the content of TPS in the compositions can reach 40-60 wt.% [9], [10]. Therefore, the purpose of this work is to improve the technology for creating biodegradable film compositions intended for use as packaging materials and to draw up a basic technological scheme for the production of biodegradable hybrid compositions (BGC).

### MATERIALS AND METHODS

The materials used were: high-grade corn starch (GOST 32159-2013); corn amylopectin starch according to GOST 32159-2013, wheat starch according to GOST 31935-2012.; pea starch (certificate of conformity, ROQUETTE, France); rice starch (LLC Vinh Thuan Trading Import-Export Co. Ltd (Vietnam), (JSC Bioprogress, Moscow, Russia); distilled glycerin grade PK-94 (GOST 6824-96); crystalline sorbitol; low density polyethylene (high pressure) grade 11503-070



produced by Kazanorgsintez PJSC (Russia); dry vermicompost according to GOST R 56004-2014; TU 9818-001-47294670-2015 glycerin, sorbitol.

Organoleptic evaluation of polymer films according to the norms of SanPiN 42-123-4240-86, GN 2.1.6.695-98, SanPiN 2.1.4.559-96. The breaking stress in tension and the relative elongation at break of the films from the compositions were determined at a temperature of  $23 \pm 2^\circ\text{C}$ , a relative humidity of  $50 \pm 5\%$ , and a speed of expansion of the clamps of the testing machine in accordance with GOST 14236-81. The experiment was carried out on a tensile testing machine RM-50. The limit of the permissible value of the load measurement error did not exceed  $\pm 1\%$ . Determination of vapor permeability according to GOST 33355-2015 (ISO 7783: 2011). Evaluation of biodegradation according to the modified Sturm method GOST 32433-2013. Water absorption was calculated according to where  $m$ ,  $m_1$  are the mass of the dried sample and the mass of the sample after exposure in water, respectively, g, using an analytical electronic balance ViBRA AF-R220E (ViBRA SHINKO) according to GOST 24104-88.

## AS A RESULT OF RESEARCH

The All-Russian Research Institute of Starch Products is conducting research on the use of starch to obtain biodegradable polymer products. The process of modification of various types of starches by the extrusion method in the presence of plasticizing agents has been investigated. The parameters of the technological regime for obtaining thermoplastic starch (TPS) have been developed. Mathematical models of optimal compositions of biohybrid compositions (BHC) based on polyethylene and TPK have been created, depending on the technological modes of film production. The physical and mechanical characteristics of BGC and the film were investigated at various ratios of components and the effect of ultrasonic treatment (US), considering the standard values of the maximum stress and elongation at break. During storage of BGK and films in bio humus, physical and mechanical properties were determined, indicating the accelerated decomposition of products. The microstructure of polyethylene-starch compositions obtained at different temperatures has been studied, an improvement in consumer and operational characteristics when exposed to the ultrasonic treatment of the composition due to more uniform distribution of components in the polymer matrix has been established.

The use of montmorillonite in the production of biodegradable film materials imparts hydrophobicity and makes it possible to significantly improve the physical and mechanical characteristics of film and other materials and allows to reduce the proportion of polyethylene by 2 times or more, which increases the biodegradability of polymer products.

A comprehensive study of the effect of the type of packaging on the processes of moisture migration, changes in lipase activity and microbiological indicators was carried out. It is shown that a new type of biodegradable packaging based on thermoplastic starch has similar barrier properties in comparison with classical polypropylene packaging, while the quality of the packaged products is guaranteed by the example of jelly marmalade glazed with confectionery glaze.

### NATURAL ADDITIVES FOR BIODEGRADABLE MATERIALS

In his article, the author Sagdat Tazhibaeva [11] Assume a Gaeta that for regulation of structural and mechanical properties of the films proposed to use salts of calcium and magnesium. Influence of calcium and ions on strength and deformation characteristics. And they monotonously increase the strength characteristics of starch-agar films, and the curves of changes in these parameters in the presence of magnesium have a maximum at a concentration of 0.5%. The difference in the effect of ions on the structural and mechanical properties of the films is explained by the degree of hydration of these ions. The biodegradability of starch-agar films was controlled by the authors by changing their IR spectra. The most significant changes are observed in the intensity and localization of the peaks corresponding to the OH, CH, and CC bonds, which may indicate a change in the structure of the films due to the destruction of the network of hydrogen bonds and hydrophobic interactions, as well as the rupture of hydrocarbon chains and the destruction of the framework of carbohydrate molecules.

Josue Hernandez-Varela [12] The world is currently confronted with the effects of pollution from petroleum-derived plastics (plates, glasses, cutlery), prompting the search for new biodegradable materials based on agro-industrial lignocellulose residues that help reduce their use and create more safe waste for the environment The use of garlic peel (GS) as a raw material in the form of cellulose microfibrils (CMF) and as a precursor of cellulose insulation to obtain microcrystalline cellulose (MCC) for the manufacture of the biodegradable composite film is presented below. To obtain biodegradable films, mixtures of potato starch, gellan gum and glycerin with CMF were used for future use as food utensils; on the other hand, chitosan (Q), alginate (A) and MCC were used to obtain a film capable of removing dyes from water and absorbing gases. These CMFs were used to make biodegradable films for food utensils, and garlic peel nanoparticles (CNP-GS) were used to remove the dye films. Both materials were easily analyzed using scanning electron microscopy (SEM) as a powerful technique for evaluating the surface and cross-section of materials and understanding the location of polymers.

A.S. Mohammed and al. [13]. The natural or hydrolyzed starch and mate extract (10 wt. % Or 20 wt. %) Phi investigated films obtained by extrusion and compression. Natural starch-based material (TPNS) showed lower water vapor permeability and higher Young's permeability. 's Modulus (I) compared to matrix hydrolyzed starch (TPHS), but deformation decreases with break ( $\epsilon b$ ) and toughness (T). The inclusion of 10 wt. The % extract in TPNS resulted in higher I and  $\epsilon b$  and the result was the most hydrophobic material. In contrast, TPHS with 20 wt %. The additive gives phi I with the highest  $\epsilon b$  and T, indicating the plasticizer e ff action of the extract in this concentration and system. All materials disintegrated after 10 weeks of burial, helping to reduce the amount of waste. The biodegradable film containing extract mate yerba demonstrated antioxidant activity and color variation in different pH, indicating that they are promising as an active role in the intellectual and packaging for food products in accordance with the new trends in the field of biodegradable and functional packaging.



## **ADDITIVES IN NON-NATURAL BIODEGRADABLE MATERIALS**

Jordana Corralo Spada. [14] Among petroleum-based packages, the use of expanded polystyrene (EPS) stands out, which is characterized by low production costs, low density, high moisture resistance and dimensional stability. However, improper disposal and the complexity of their recycling together with their non-biodegradability can lead to serious environmental problems. Knowing that it is impossible to discourage the use of this material by the public, the present study focused on the production of environmentally friendly foams based on cassava starch and rice hulls (RH). Compared to EPS, materials developed using biopolymers are less flexible and more sensitive to water. The addition of rice hulls improved mechanical properties and reduced density and water absorption compared to foams made using starch alone. Foams were produced by temperature and pressure and it was investigated the effect of various proportions of relative humidity (0,20,40 and 60% (wt/ Wt.)). The higher the relative humidity, the higher the density and the lower the water absorption capacity (WAC). Maximum tensile stress and tensile strain were negatively affected by the addition of 60% (w / w) RH. In contrast to the maximum bending stress, this was influenced positively. In addition, sorption isotherms showed that 40% and 60% RH samples adsorbed less water compared to unfilled foam. The 60% RH formulation was chosen for storing cherry tomatoes because of its higher maximum flexural stress and lower WAC, which is considered a promising material, the higher the density and the lower the water absorption capacity (WAC). At the maximum tensile stress and tensile strain negatively claim ovliyala additive 60% (wt. / Via).

Graft copolymerization was initiated with cerium ammonium nitrate (CAN) or potassium persulfate (KPS) resulting in modern reaction mechanisms. For each of the three initiators diByli used various synthetic routes. The structures of the new SAP on a biological basis have been characterized using IR spectroscopy. Thermogravimetric measurements were performed to check thermal stability, and the morphology of the samples was examined using scanning electron microscopy (SEM). Physicochemical measurements were performed to characterize the properties of new materials. The water absorption capacity of the obtained hydrogels was measured in distilled water and 0.9% NaCl solution.

Jordana Corralo Spada. Among petroleum-based packages, the use of expanded polystyrene (EPS) stands out, which is characterized by low production costs, low density, high moisture resistance and dimensional stability. However, improper disposal and the complexity of their recycling together with their non-biodegradability can lead to serious environmental problems. Knowing that it is impossible to discourage the use of this material by the public, the present study focused on the production of environmentally friendly foams based on cassava starch and rice hulls (RH). Compared to EPS, materials developed using biopolymers are less flexible and more sensitive to water. The addition of rice hulls improved mechanical properties and reduced density and water absorption compared to foams made using starch alone. The foams were obtained

by thermal pressing and the effect of different proportions of relative humidity (0, 20, 40 and 60% (w/w)) was investigated. The higher the relative humidity, the higher the density and the lower the water absorption capacity (WAC). Maximum tensile stress and tensile strain were negatively affected by the addition of 60% (w/w) RH. In contrast to the maximum bending stress, which was influenced positively. In addition, sorption isotherms showed that 40% and 60% RH samples adsorbed less water compared to unfilled foam. The 60% RH formulation was chosen for storing cherry tomatoes because of its higher maximum flexural stress and lower WAC, which is considered a promising material, the higher the density and the lower the water absorption capacity (WAC). The maximum tensile stress and tensile strain were negatively affected by the addition of 60%.

Elzbieta Czarnecka [15]. Superabsorbent polymers (SAP) based on biopolymers are being synthesized and investigated as a biodegradable alternative to fully synthetic SAP, especially based on acrylic acid and its derivatives. This article focuses on the chemical modification of starch (S) and the synthesis of new potentially biodegradable polymers using acrylic acid (AA) as a side chain monomer and crosslinking mediator together with N, N'-methylenebisacrylamide (MBA).

## CONCLUSION

The main essence of the studies studied is the fact that every year the study and development of biodegradable polymers becomes an important and necessary trend.

The practical widespread use of biodegradable films to produce packaging materials presents a real opportunity to save resources and minimize damage to the environment from the growing and irreversible harmful effects of solid household waste. Change in the chemical structure of synthetic non-degradable polymers because of the introduction of natural additives into the film, including thermoplastic starch affects the fragmentation of packaging polymers in soil. Therefore, the use of biodegradable polymer products for packaging various types of food products requires further research.

## REFERENCES

- [1] Kolpakova V.V., Usachev I.S., Sardzhveladze A.S., Solomin D.A., Ananiev V.V., Vasiliev I.Yu. Improving the technology of using thermoplastic starch for biodegradable polymer films : Food industry. 2017. No. 8 . S. 34-38 .
- [2] Kolpakova V.V., Usachev I.S., Solomin D.A. Biodegradable polymers: composite biocomponents and technological solutions for production : Food industry . 2019. No. 12 . S. 51-57.
- [3] Kaseem, M., Hamad, K. & Deri, F. Thermoplastic starch blends: A review of recent works: Polym. Sci. Ser. A 54, 165–176 (2012).

[4] Lukin N.D, Usachev I.S. Technology for obtaining thermoplastic starches: Bulletin of the Voronezh State University of Engineering Technologies. - 2015. - Issue. 66. - No. 4. - P. 156-159.

[5] Lukin D. Application of thermoplastic starch and starch containing waste of food industry in biodegradable polymer compositions. D. Lukin , V. Kolpakova , V. Ananyev , N. Lukin , I. Usachev , A. Sardjveladze and D. Solomin. Proceedings of the 12th International Conference on Polysaccharides-Clycoscience : Prague, 19–21 th Oktober 2016. PP. 58-62.

[6] Kodsangma, A. Effect of sodium benzoate and chlorhexidine gluconate on a bio-thermoplastic elastomer made from thermoplastic starch-chitosan blended with epoxidized natural rubber / A. Kodsangma , Na. Homsaard , S. Nadon , P. Rachtanapun , N. Leksawasdi , et. al. // Carbohydrate Polymers. - 2020. - V. 242 . - No. 15. - P. 116421. <https://doi.org/10.1016/j.carbpol.2020.116421>

[7] Theeraphorn, P. Effects of acetylated and octenyl- succinated starch on properties and release of green tea compounded starch / LLDPE blend films / P. Theeraphorn , K. Thomas, H. Nathdanai // Journal of Food Engineering. - 2020. - V. 284. - P. 110057. [doi.org/10.1016/j.jfoodeng.2020.110057](https://doi.org/10.1016/j.jfoodeng.2020.110057)

[8] Noivoil, N. Compatibility improvement of poly (lactic acid) / thermoplastic starch blown films using acetylated starch / N. Noivoil , R. Yoksan // Journal of Applied Polymer Science. - 2020. - V. 138 - No. 2. - P. 49645. <https://doi.org/10.1002/APP.49675>

[9] Sagdat Tazhibayeva// Preparation And Regulation of Structuralmechanical Properties Of Biodegradable Films Based On Starch And Agar // Eastern-European Journal of Enterprise Technologies DOI: 10.15587 / 1729-4061.2020.213226

[10]10. Josué hernández-varela // biodegradable polymers: new alternatives using nanocellulose and agroindustrial residues // microsc . Microanal . 26 (suppl 2), 2020

[11].A S. Mohamed // ion conduction in chitosan-starch blend-based polymer electrolyte with ammonium thiocyanate as charge provider // journal of polymer research (2020) 27: 149; <https://doi.org/10.1007/s10965-020-02084-7>

[12]Josue Hernandez-Varela Biodegradable polymers: new alternatives using nanocellulose and agroindustrial residues // Microscopy and Microanalysis , Volume 26 , Supplement S2 , August 2020 , pp. 356 - 359

[13]A.S. Mohammed and al. [13] The influence of raster angle and moisture content on the mechanical properties of pla parts produced by fused deposition modeling // Polymers 2021, 13(2), 237; <https://doi.org/10.3390/polym13020237>

[14]Jordana Corralo Spada // Biodegradable Cassava Starch Based Foams Using Rice Husk Wastes Macro Filler // Waste and Biomass Valorization (2020) 11: 4315- 4325; <https://doi.org/10.1007/s12649-019-00776-w>

[15] Elżbieta Czarnecka et al. // Semi-Natural Superabsorbents Based on Starch-g-poly(acrylic acid): Modification, Synthesis and Application // *Polymers* 2020, 12 (8) <https://doi.org/10.3390/polym12081794>.