The Austrian Journal of Technical and Natural Sciences, No 1–2
ISSN 2310-5607

PREMIER Publishing
ppublishing.org

DOI:10.29013/AJT-25-1.2-19-26

STUDY OF SPECIFIC PROPERTIES OF THE OXIDIZED RICE STARCHES MODIFIED WITH DIFFERENT OXIDANTS AND ELECTROCHEMICAL METHOD

Sharipov Muzafar [1]

[1] Department of Chemistry and oil-gas technologies, Bukhara state university

Cite: *Sharipov M. (2025). Study of specific properties of the oxidized rice starches modified with different oxidants and electrochemical method. Austrian Journal of Technical and Natural Sciences 2025, No. 1–2.* https://doi.org/10.29013/AJT-25-1.2-19-26

Abstract

The physicochemical properties of native rice starch, electrochemical modified rice starch and oxidized rice starch were also studied parallel using rapid visual analysis (RVA), X-ray diffraction pattern (XRD) and dynamic rheometry. Al samples of oxidized starches showed lower swelling power (SP) and solubility and higher paste clarity in comparison with native starch. These results suggest that the undesirable properties in native, chemical and electrochemical oxidized rice starch samples could be overcome through all types of oxidation. Oxidized starch by electrochemical method showed the highest ability to resist shear of all oxidized starch samples.

Keywords: *rheology, electrochemical oxidation, gel formation, pastes clarity, swelling power*

Introduction

Oxidized starch comes from oxidation modification of original starch in order to overcome its shortcomings, such as limited hydrophilic character and chemical reactivity, poor solubility and poor functional properties (Wang Y. J., Wang L., 2003). The successful oxidation modification has made starch, which is high availability in nature, renewable and biodegradable, becomes a useful polymer in a wide range of applications (Raina C. S., Singh S., Bawa A. S., Saxena D. C., 2006). Oxidized starch shows much better water solubility, excellent film-forming properties, lower viscosity at high solid content, less retrogradation and better clarity than native starch (Kaur M., Oberoi D. P.S., Sogi D. S., Gill B. S., 2011). The unique properties of oxidized starch have diversified starch's applications in paper and textile industries for providing surface sizing and thickening properties (Singh J., Kaur L., Mc Carthy O. J., 2007).

In general, oxidized starch is prepared by reacting starch with oxidants (e.g., hydrogen peroxide, hypochlorite, periodate, ozone, bromine, chromic acid and permanganate) under certain reaction conditions (Li J., Vasanthan Th., Bressler D. C., Tyler R. T., 2010). The most common starch oxidizers used in production are sodium salts of hypochlorites and periodates, and also hydrogen peroxide (Sangseethong K., Termvejsayanon N., Sriroth K.). The mechanism of the chemical modification process with different oxidizers occurs differently. Researches the utilization of hydrogen peroxide for the oxidation of starch necessitates the presence of iron ions (Tolvanen P., Mäki-Arvela P., Sorokin A. B. Salmi T., Murzin D.Yu., 2009). Nevertheless, the oxidation process is not fully achieved, and there is limited enhancement of the adhesive properties. The utilization of potassium permanganate and sodium periodate is deemed environmentally unfriendly due to their hazardous nature, susceptibility to poisoning and explosions, difficulties in handling at elevated temperatures, and potential risks during experimental procedures (Kato Y., Matsuo R., Isogai A., 2003; Wilpiszewska K., Spychaj T., 2008).

As is known application of starch in many industries is demanded with modifying its structure and properties, and methods of modification would not change feature and individuality of this natural polymer. Among numerous ways of modifying of structure and properties of polymers chemical modification takes special place (Ashogbon A. O., Akintayo E. T., 2014). As the way of creation of materials with the improved complex of properties this way will receive development and in the further. And successes in this area first of all should be connected with the physical and chemical approach to an estimation and generalization of already existing extensive experimental and theoretical material from the point of view of the polymeric nature of reacting particles.

Some years in department of chemistry within the limits of the state project on development of technologies of reception of the modified starch, with the purpose of its application in the textile industry are conducted research. The objective of this study was to prepare the modified rice starches such as oxidized starch by various oxidants in various mediums. It was found that the levels of chemical and electrochemical oxidation used in this study did not cause any significant changes pastes clarity. Oxidized starch by chlorate showed lower ability to resist shear in comparison to native starch, while it showed higher ability to resist shear in comparison to oxidized starch by permanganate.

Material and methods

The experimental material consisted of starches of rice produced from rice flour at the Bukhara region as well as rice starch and rice flour starch. The above-mentioned starches were subjected to the oxidation process by means of three methods: 1. Starch subjected to electrochemical processing was performed according to Litvyak *et al.* (Litvyak V. V., Lovkis Z. V., Rebenek E. V., Kupchik M. P., 2007). Briefly, laboratory electrolyze represents electrolyze cell with the anode and the cathode, made of stainless steel, In quality anolite 25%-s' starched suspension acted, in quality catolite were used – 4% th solutions NaCl. Electrochemical processing spent during 60 mines at the force of current 0,6 A. The constant value of force of in currents of 1 hours supported by gradual reduction of pressure by electrodes with 220 to 50 V. Modification was performed at the temperature 25–35 °C.

2. Permanganate oxidation of starch. The cleared suspension of starch containing 25% of solids moves in a vessel of continuous action. Before suspension into a vessel enter the set quantity of sulfuric acid, and then permanganate of potassium. Suspensions maintain temperature in a reactor 30–40 °C for what provide heating of initial suspension to the specified temperature. The expense of sulfuric acid about 1–2% to suspension solids, permanganate of potassium 0,1–0,2%. Time of stay of suspension in a vessel makes about 2 hours that provides end of reaction of oxidation and disappearance of coloring of the suspension appearing after introduction of an oxidizer. After the termination of reaction suspension will partially neutralize a solution кальцинированной soda and simultaneously dilute to concentration of 10%.

3. Modification with sodium chlorate(I) was performed according to methodology of Forsell *et al.* (Forssell P., Hamunen A., Autio K., Suortti P., Poutanen K., 1995). Briefly 400 g of starch was dispersed in water to give 25% suspension. After the addition of 4 g of sodium chlorate(V) solution was performed at room temperature by mixing the starch suspension in alkaline medium (pH=10.0) for 60 min and subsequent neutralization of the reaction mixture with 1 mol/L H_2SO_4 solution to reach pH=7.0. Modification was performed at the temperature 35–45 °C.

Then, the modified starches were washed, dried, disintegrated, and sieved. Starch oxidation was performed according to procedure which was optimalized in previous trials (ISO Norm 112144, 1996); (2) the content of aldehyde groups, according to Zhang (Zhang L., Liu P., Wang Y., Gao W., 2011); (3) The pasting properties of rice starch were measured according to our previous method by using a Rapid Visco Analyzer (Thermo Scientific, HAAKE); (4) X-ray diffraction (XRD) patterns of the samples were characterized by an XRD-6100 instrument (Shimadzu) Sample preparation was carried out were made by cold pressing of the polymer in the form of monolithic round tablets 2 mm and a diameter of 18 mm.

Results and discussion

Analyze of functional group on modified rice starches

In the process of starch oxidation, the destruction of its macromolecules occurs simultaneously with oxidation. Under the action of an oxidizing agent, hydroxyl groups are converted into aldehyde groups, and with further exposure to an oxidizing agent, the latter are oxidized to carboxylic acid groups (Table 1).

Table 1. *Content of carboxyl groups (%) and aldehyde groups (g CHO/100 g d.w.) in oxidised starches*

Starch samples (temp. of oxidation, °C)	Carboxyl groups in oxidised starches (%±SD)		Aldehyde groups in oxidised starches (%±SD)	
Electrochemical oxi-dized (with NaCl sol.)	0.018±0.003 (25 °C)	0.061±0.003 (35 °C)	0.102±0.0052 (25 °C)	0.157±0.0027 (30 °C)
Oxidized by perman-ganate of potassium	0.301±0.017 (30 °C)	0.433±0.029 (40 °C)	0.021±0.0012 (35 °C)	0.079±0.004 (40 °C)
Oxidized by sodium chlorate (V)	0.226±0.005 (35 °C)	0.380±0.011 (45 °C)	0.014±0.0001 (40 °C)	0.053±0.0015 (45 °C)

The only exception was rice starch in which the highest number of carboxyl groups was observed upon modification with permanganate. Oxidant amount is an important part in the oxidant preparation of starch program. For it directly influence the molecular structure change of carboxyl content and oxidation starch (Halal S. L. M., Colussi R., Pinto V. Z., Bartz J., Radunz M., Carreño N. L.V., Dias, A.R.G., Zavareze E. R., 2015). It has been established that the content of carbonyl (–CHO$^-$) and carboxyl (–COOH$^-$) groups characterizes the degree of oxidation and degradation of starch macromolecules. In this regard, the content of carbonyl and carboxyl groups in starch samples isolated with different degrees of oxidation was changed. Analysis of the content of carbonyl and carboxyl groups is carried out according to the methods described.

An analysis of the results compiled for the content of aldehyde groups (Table 1) enables concluding that rice starch was the most susceptible to hydrolysis with the electrochemical method, as it was characterized with the highest increment of aldehyde groups compared to the other methods. Compared to the other methods, permanganate caused the lowest rise in the number of aldehyde groups, which confirms the results of our previous investigations (Sanchez-Rivera M. M., Garcia-Suarez F. J. L., Velazquez del Valle M., Gutierrez-Meraz F., Bello-Perez L. A., 2017).

Gel formation

Starch gelation is complex process involving three main stages. First, starch grains swell reversibly by attaching a small amount of water. When the temperature rises, a large amount of water is added, accompanied by a strong swelling of the grains with an increase in their volume by hundreds of times and an increase in the viscosity of the solution; this stage is irreversible. Swelling of starch occurs due to rupture of hydrogen bonds and hydration of polysaccharide macromolecules. At the last stage, soluble polysaccharides are extracted with water, the grains lose their shape, turning into bags suspended in solution. This starch gel structure is the primary structure (Kuakpetoon D., Wang Y., 2006).

Experiments conducted on the functional properties of our modified rice starch have indicated some similarities with corn or wheat starches (Sasaki T., 2005). Oxidized rice starch with chlorate salts paste presents a fibrous rheology similar to corn starch paste. Starch hydrogels are a typical example of systems exhibiting non-Newtonian liquid properties (Sharipov M. S., 2022). Compositions of unmodified rice starches are highly structured. The maximum permissible concentration for native rice starch during gel formation turned out to be 5% (m / v) but for oxidized rice starch 7% (m / v) and the effect of concentration in this process is shown in Figure 1. Oxidized rice starch hydrogels also showed average transparency properties in pastes compared to wheat and corn starch. In hot conditions (90 °C) the paste of the native rice starch was completely transparent, but in cold conditions (15 °C) the paste was very opaque.

Figure 1. *Chilled hydrogels of rice starch (bottom oxidized) and native (top unoxidized) (obtained from 5, 6, 7% pastes, respectively)*

However, the modified starch pastes were transparent in both states. Freeze thaw stability is an important aspect regarding the characterization of starches (Beninca C., Colman T. A.D., Lacerda L. G., Carvalho-Filho M. A.S., Demiate I. M., Schnitzler E., 2013).

It has been established that electrochemical treatment of a starch suspension makes it possible to obtain starch, which forms a transparent paste that is not prone to gelation. In oxidized starches, a decrease in the tendency of the paste to retrogradation is observed, which is noticeable in comparison with native (unmodified starches) (Fig. 2). Electrochemically oxidized rice starch hydrogels are a typical example of systems exhibiting non-Newtonian liquid properties.

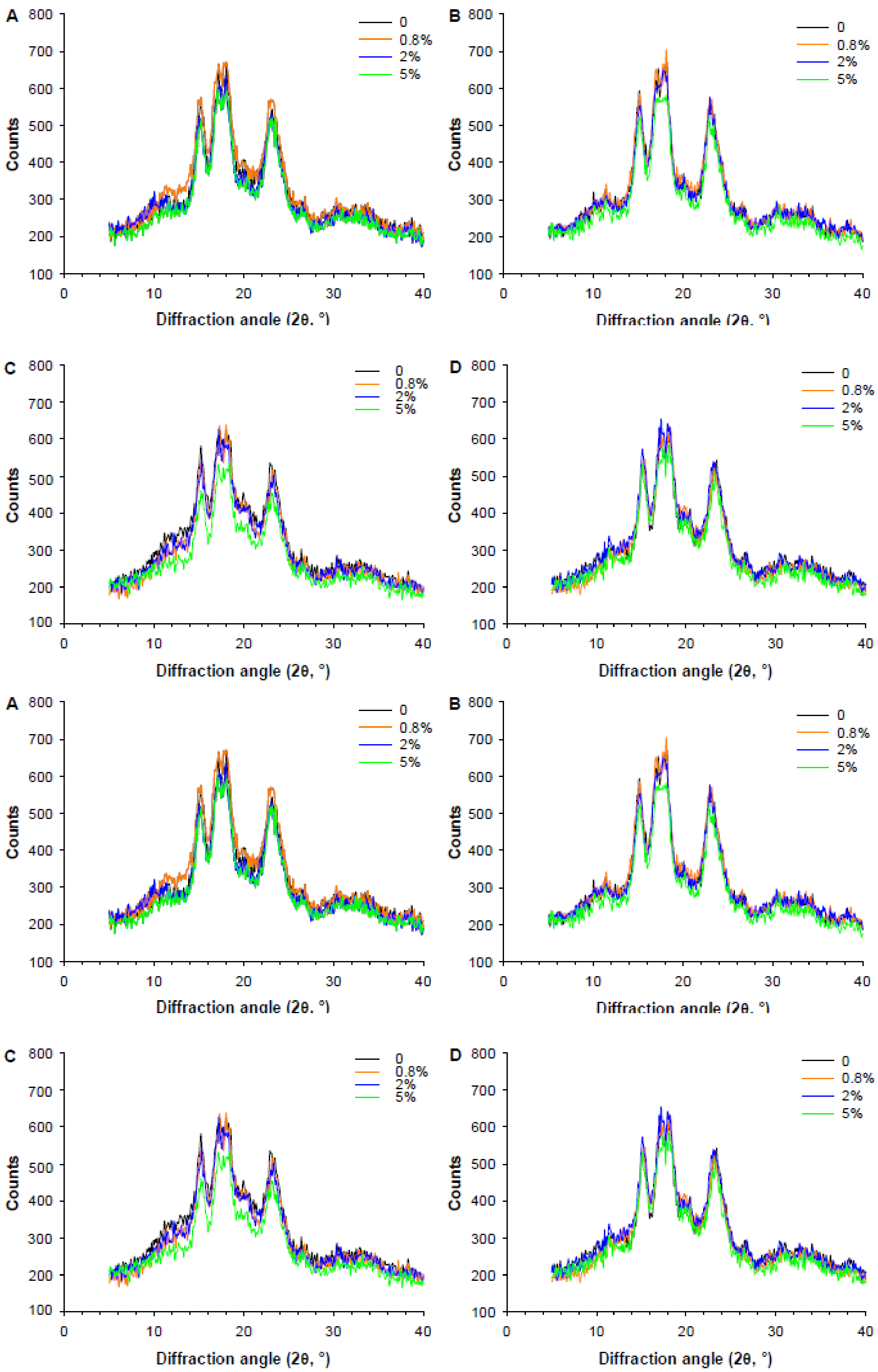
Figure 2. *Pastes of native (top) and electrochemically modified (bottom) rice starch*

Hydrogels of modified rice starches are highly structured. In hot conditions (70 °C) the native starch paste was completely transparent, but in cold conditions (–5 °C) the paste was very opaque. However, the modified starch pastes were transparent in both states. Freeze thaw stability is an important aspect regarding the characterization of starches. These changes (along with decrease in molecular weight) cause a decrease in the gelatinization temperature and viscosity of starch pastes.

X-ray analysis

In the process of starch oxidation, changes occur both in the amorphous and in the crystalline regions of the starch grain. This re-echoed the accepted fact that cross-linking mainly take place in the amorphous regions of the starch granules and did not alter the crystalline patterns of starches. In this case, an increase in the degree of crystallinity of oxidized starch is observed (Tillayeva D. M., Sharipov M. S., 2021). Analysis results are shown in figure 3.

Figure 3. *X-ray diffraction results of native (a) and oxidized rice starch's modification product of its oxidation by electrochemical method (b) chlorate of sodium (c) and permanganate (d)*

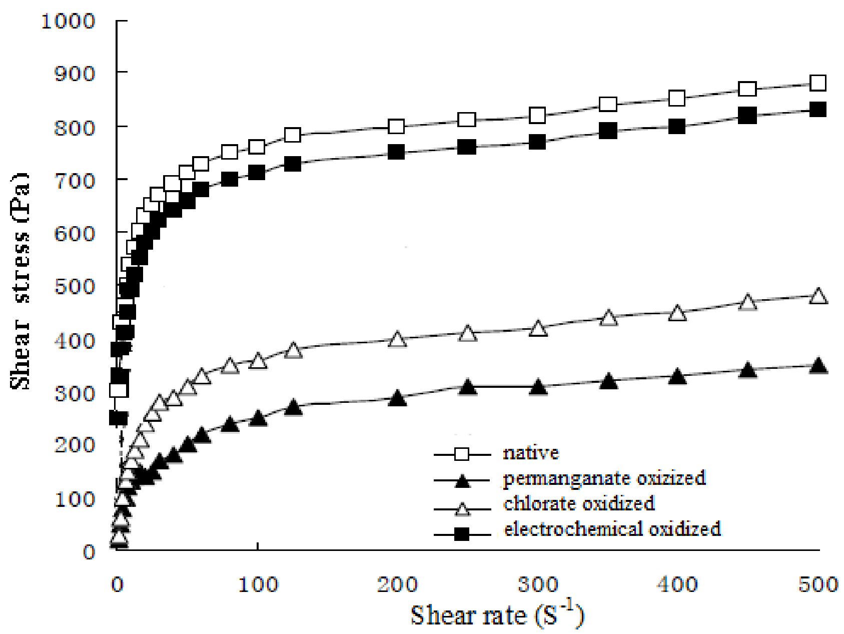


X-ray structural analysis showed that during the oxidation of rice starch by electrochemical and chemical oxidation, changes in the supramolecular structure of starch are insignificant: a slight decrease in the degree of crystallinity is observed starch after its oxidation, which manifests itself in a decrease in the intensity of reflexes at angles of 19.5 and 22.0 degrees (Fig. 3). As a result of the gelation process, an increase in the hydration and mobility of the chains of macromolecules takes place (Tillayeva D. M., Sharipov M. S., 2023). In a later work, using high and low angle X-ray diffraction methods, the researchers discovered disk-like regions with increased electron density, having a crystalline structure of β-form of amylose, in destructive starch gels (Zhong Y., Tai L., Blennow A., Ding L., Herburger K., Qu J., Xin A., Guo D., Hebelstrup K. H., Liu X., 2022). The degree of crystallinity of the gels was 16–22% as shown. The authors believe that the sol-fractions of the molecule are hydrated, and double helices are formed upon dehydration of long segments of branched and linear molecules. Above the critical concentration, double helices aggregate, forming crystal cores that grow into disk-like regions (Pfister B., Zeeman S. C., 2016).

Flowing Characteristics

The results from the previous studies indicated that rice starch samples were pseudoplastic and shear thinning liquids. As shown by the flow curves in Figure 4, shear stress of all native and modified starch samples increased with increasing shear rate.

Figure 4. *Shear stress as a function of shear rate for native and oxidized rice starch samples*



At the same shear rate, native starch showed the highest shear stress, while oxidized starch with permanganate showed the lowest shear stress. Gibinski et al. indicated that high values of shear stress pointed to a high stability of the structure of the starch (Gibinski M., Kowalski S., Sady M., Krawontka J., Tomasik, P., Sikora M., 2006). According to these authors electrochemical modified starch had the most stable structure and the strongest ability to resist shear, the structure of oxidized starch was weakened and lost the ability to resist shear.

Conclusion

However, a partially degraded network was not resistant to shear and could not maintain the integrity of starch granules after oxidation by permanganate, resulting in a decrease in shear stress. Oxidized starch by chlorate showed lower ability to resist shear in comparison to native starch, while it showed higher ability to resist shear in comparison to oxidized starch by permanganate.

Oxidized starch by electrochemical method showed the highest ability to resist shear of all oxidized starch samples. The reaction order of oxidized modification had a significant influence on the physicochemical proper of starch granules.

References

Wang Y. J., Wang L. Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite // *Carbohydrate Polymers*. 2003. – 52. – P. 207–217.

Raina C. S., Singh S., Bawa A. S., Saxena D. C. Some characteristics of acetylated, cross-linked and dual modified Indian rice starches // *European Food* Research and *Technology*. 2006. – 223. – P. 561–570.

Kaur M., Oberoi D. P.S., Sogi D. S., Gill B. S. Physico-chemical, morphological and pasting properties of acid treated starches from different botanical sources. *Journal* of *Food Science* and *Technology*. 2011. – 48. – P. 460–465.

Singh J., Kaur L., McCarthy O. J. Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications. – A review. *Journal Food Hydrocolloids*. 2007. – 21. – P. 1–22.

Li J., Vasanthan Th., Bressler D. C., Tyler R. T. Binding of amino acids to hypochlorite-oxidized potato starch. Stach / Starke, 2010. – V. 62(9). – P. 467–474.

Sangseethong K., Termvejsayanon N., Sriroth K. Characterization of physicochemical properties of hypochlorite- and peroxide-oxidized cassava starches. *Carbohydrate Polymers,* 2010. – Vol. 82. – No. 2. – P. 446–453.

Tolvanen P., Mäki-Arvela P., Sorokin A. B. Salmi T., Murzin D. Yu. Kinetics of starch oxidation using hydrogen peroxide as an environmentally friendly oxidant and an iron complex as a catalyst. Chemical Engineering Journal, 2009. – V. 154(1–3). – P. 52–59.

Kato Y., Matsuo R., Isogai A. Oxidation process of water-soluble starch in TEMPO-mediated system. Carbohydrate Polymers, 2003. – V. 51(1). – P. 69–75.

Wilpiszewska K., Spychaj T. Chemiczna modyfikacja skrobi na drodze reaktywnego wytlaczania. *Polimery.* 2008. – V. 53. – No. 4. – P. 268–275.

Ashogbon A. O., Akintayo E. T. Recent trend in the physical and chemical modification of starches from different botanical sources: A Review. Starch-Starke. 2014. – V. 66. – P. 41–57.

Litvyak V. V., Lovkis Z. V., Rebenek E. V., Kupchik M. P. Modification of potato starch by the electrochemical method and studying of its physical and chemical properties / Vesti NAS Belarus. Seriya Agrarian Science – No. 4. 2007. – P. 109–115.

Forssell P., Hamunen A., Autio K., Suortti P., Poutanen K. Hypochlorite Oxidation of Barley and Potato Starch. Starch / Starke, 1995. – V. 47(10). – P. 371–377.

ISO Norm 112144:1996. Modified Starch – Determination of Carboxyl Group Content of *Oxidized Starch*. American National Standards Institute (ANSI), 2007. – 24 p.

Zhang L., Liu P., Wang Y., Gao W. Study on physico-chemical properties of dialdehyde yam starch with different aldehyde group contents. Thermochimica Acta, 2011. – V. 512(1–2). – P. 196–201.

Xiao H., Lin Q., Liu G. Q. Effect of cross-linking and enzymatic hydrolysis composite modification on the properties of rice starches // *Molecules* 2012. – 17. – P. 8136–8146.

Halal S. L.M., Colussi R., Pinto V. Z., Bartz J., Radunz M., Carreño N. L.V., Dias, A.R.G., Zavareze E. R. Structure, morphology and functionality of acetylated and oxidised barley starches, Food Chem., 2015. – V. 168. – P. 247–256.

Sanchez-Rivera M. M., Garcia-Suarez F. J. L., Velazquez del Valle M., Gutierrez-Meraz F., Bello-Perez L. A. Partial characterization of banana starches oxidized by different levels of sodium hypochlorite // *Carbohydrate Polymer,* 2005. – 62. – P. 50–56.

Kuakpetoon D., Wang Y. Structural characteristics and physicochemical properties of oxidized corn starches varying in amylose content // *Carbohydrate Research*, 2006. – 341. – P. 1896–1915.

Sasaki T. Effect of wheat starch characteristics on the gelatinization, retrogradation, and gelation properties // *Japan Agricultural Research Quarterly,* 2005. – 39. – 4. – P. 253–260.

Sharipov M. S. Study of changes in the properties of starch during oxidation in the creation of a component of adhesive material for surface treatment of paper // Journal of Chemistry and Technologies, 2022. – 30(1). – P. 69–78.

Beninca C., Colman T. A.D., Lacerda L. G., Carvalho-Filho M. A.S., Demiate I. M., Schnitzler E. Thermal, rheological, and structural behaviors of natural and modified cassava starch granules, with hypochlorite solutions, J. Therm. Anal. Calorim., 2013. – 111. – P. 2217–2222.

Tillayeva D. M., Sharipov M. S. Study of the influence of oxidative modification on the properties of starch with the purpose of preparation on its basis of adhesive materials for surface adhesive paper//Development of Science and Technology, 2021. – No. 3. – P. 87–88.

Tillayeva D. M., Sharipov M. S. starch oxidation and study of changing its properties for use as an adhesive component for the production of corrugated cardboard// E3S Web of Conf. Volume 402, 2023 International Scientific Siberian Transport Forum – Trans Siberia 2023. – 07033.

Zhong Y., Tai L., Blennow A., Ding L., Herburger K., Qu J., Xin A., Guo D., Hebelstrup K. H., Liu X. High amylose starch: Structure, functionality and applications, Critical Reviews in Food Science and Nutrition, 2022. – 63(1). – P. 1–23.

Pfister B., Zeeman S. C. Formation of starch in plant cells. Cellular and Molecular Life Sciences, 2016. – V. 73(14). – P. 2781–2807.

Gibinski M., Kowalski S., Sady M., Krawontka J., Tomasik, P., Sikora M. Thickening of sweet and sour sauces with various polysaccharide combinations. Journal of Food Engineering. 2006. – 75. – P. 407–414.

submitted 14.02.2025;
accepted for publication 28.02.2025;
published 28.03.2025

Contact: m.s.sharipov@buxdu.uz