

UDC 544.773.432;547.995.1

*O.A. Kostyk, O.H. Budishevska, V.B. Vostres, Z.Y. Nadashkevych, S.A. Voronov***CATIONATION OF STARCH WITH AN AMINATING REAGENT BASED ON TRIETHYLAMINE AND EPICHLOROHYDRIN****Lviv Polytechnic National University, Lviv, Ukraine**

This article presents a simplified method for the preparation of cationic starches with a different degree of substitution using triethylamine and epichlorohydrin as starting materials. The optimal conditions for a starch cationation by a semi-dry method have been determined. The cationic starch with quaternary ammonium cation groups was prepared by the interaction of an aminating reagent with corn starch in the presence of sodium hydroxide. The aminating reagent, 3-chloro-2-hydroxypropyltriethylammonium chloride, was synthesized by the one-pot interaction between triethylamine and HCl followed by the reaction with epichlorohydrin in the presence of cetyltrimethylammonium bromide as a catalyst. The cationic starches were fabricated with the degree of substitution of hydrogen atoms in starch hydroxy groups equal to 0.02–0.45. The effects of molar ratios of sodium hydroxide to the aminating reagent and the aminating reagent to starch (with respect to a D-glucopyranose unit) in the initial reaction mixture on the degree of substitution were investigated. It was shown that the cationic starch with the highest degree of substitution was formed at an optimal starting molar ratio of sodium hydroxide to the aminating reagent that is equal to 1.2–2.0. An increase in the molar ratio of aminating reagent to starch significantly increases the degree of substitution when the content of sodium hydroxide is less than the optimal value. The reaction efficiency of the cationation of corn starch decreases with an increase in the molar ratio of aminating reagent to starch (in the test range of 1.0 to 6.0).

**Keywords:** cationic starch, aminating reagent, degree of substitution, triethylamine, epichlorohydrin.

**DOI:** 10.32434/0321-4095-2019-127-6-113-120

**Introduction**

Natural raw materials, such as carbohydrates (cellulose, starch, chitin, chitosan, etc.) are of great interest to create new materials. Annually, the plants produce around  $10^{11}$  tons of polysaccharides via photosynthesis. Since the resources are abundant and renewable, it is reasonable to modify them to obtain biodegradable materials that conform to the environmental safety regulations better than synthetic materials.

Amino carbohydrates are the most interesting with respect to their application in food, cosmetic, pharmaceutical industries, agriculture and medicine; they include such polysaccharides as chitin, chitosan [1] and cationic starches [2,3]. The presence of amino groups provides ability to form complexes with heavy metals and toxins [4], harmlessness, biocompatibility, and good clinical and bactericidal properties [5].

There are currently some methods for the production of cationic starches, which are mainly used as colloid flocculants in paper and textile manufacture. Polyelectrolyte complexes for the formation of hydrogels and dispersions are prepared by a combination of cationic polysaccharides with anionic polyelectrolytes [6]. However, the modified starches with amino groups did not widely used in food, cosmetic and pharmaceutical industries.

Thus, it is important to search for new simple and effective methods for the synthesis of cationic starches and materials on their basis, which are relevant to cosmetics and medicine.

In general, the reagents which can be used for the starch cationation are quaternary ammonium salts with a reactive terminal group, e.g. 3-chloro-2-hydroxypropyltrimethylammonium chloride, 2,3-epoxypropyltrimethylammonium chloride [3,7],

and 2,3-epoxypropyltrimethylammonium acetate [8,9]. They are commercially available either in a chlorohydrin or in a reactive epoxide form. However, it is necessary to mention that the above reagents are too expensive. That is why the development of new economically attractive methods for the starch cationation is still an actual problem.

The purpose of this work is to simplify the existing methods for the preparation of highly substituted starches with the use of triethylamine and epichlorohydrin as starting materials.

#### Materials and methods

Corn starch (Optima) was used as received. Epichlorohydrin (ECH) (Aldrich) was used without any purification. Triethylamine (TEA) (Aldrich) was dried over KOH and distilled. Isopropyl alcohol (Aldrich) was distilled prior to use. Sodium hydroxide (NaOH) was used as 2.0 N solution in water. Hydrochloric acid (HCl) was used as a solution in water.

The aminating reagent, 3-chloro-2-hydroxypropyltriethylammonium chloride (AR), was prepared by the reaction of triethylammonium chloride with ECH in the equimolar ratio. TEA and distilled water were placed at a 1:10 molar ratio in a reactor equipped with a reflux condenser and stirrer. 35.4% hydrochloric acid was added in the ratio of TEA to HCl=1:1.1 and the mixture was further stirred at 20°C for 30 minutes. ECH was poured into the reactor at 30°C in an equimolar ratio with respect to triethylammonium chloride followed with the addition of cetyltrimethylammonium bromide as a phase-transfer catalyst (5 wt.% with reference to the total reagent weight). The reaction mixture was agitated at 30°C and pH 8.0–8.5 for 7 hours. Subsequently, the excessive water and volatile compounds were removed in vacuo at room temperature; the reaction mixture weight was nearly the theoretically value.

The starch sample with quaternary ammonium cation groups (St–O–AR) was fabricated by the interaction of starch with the AR in the presence of NaOH by a semi-dry method.

1.0 g of starch was introduced into a reactor equipped with a mechanical stirrer; then, the calculated amount of the AR was inserted and the mixture was agitated for 10 minutes. The calculated amount of a 2.0 N aqueous solution of sodium hydroxide was added afterwards and the reaction

mixture was stirred at 40°C for 7 hours. The reaction mixture was further neutralized by a 20% aqueous solution of HCl and washed by isopropyl alcohol. The settled product was centrifuged at 2500 rpm for 15 minutes after each washing.

Thus, the St–O–AR was purified from unreacted reagents and low molecular side products by treble sedimentation. The obtained St–O–AR was either dried or dispersed in a calculated amount of water.

The nitrogen content was determined by the Kjeldahl method [10].

The degree of substitution (DS) of the replaced hydrogen atoms in the hydroxy groups of starch with amino containing fragments was defined as:

$$DS = \frac{162N}{1400 - 194N},$$

where N is the nitrogen content, wt.%.

The effectiveness of the amination (ER, %) was calculated by the formula:

$$ER, \% = \frac{DS}{AR : GU} \cdot 100\%,$$

where AR:GU is the AR:D-glucopyranose unit molar ratio in the initial reaction mixture.

The IR spectra were recorded using a Specord-80M instrument in the range of 4000 to 400 cm<sup>-1</sup> (film, KBr).

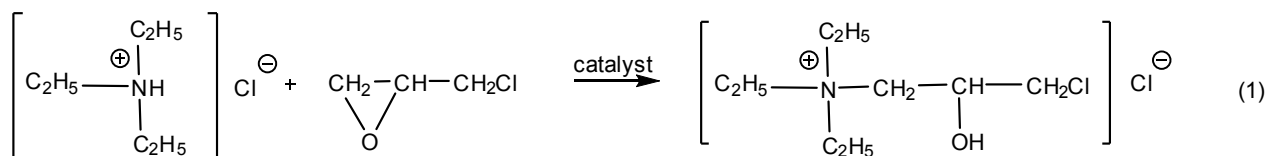
SEM microphotographs were obtained through a measuring raster electron microscope REM-106I (Selmi, Ukraine) with a high-vacuum cell using a secondary electron recording sensor at 20.0 kV accelerating voltage. The copper sputtered starch and reaction mixture samples for the SEM study were placed on copper plates.

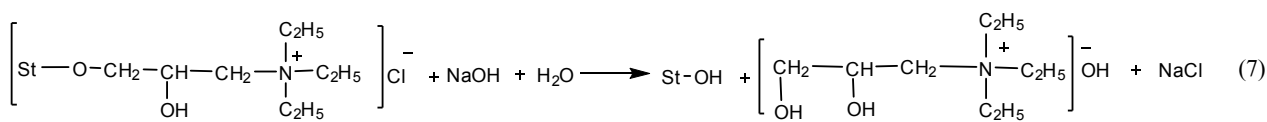
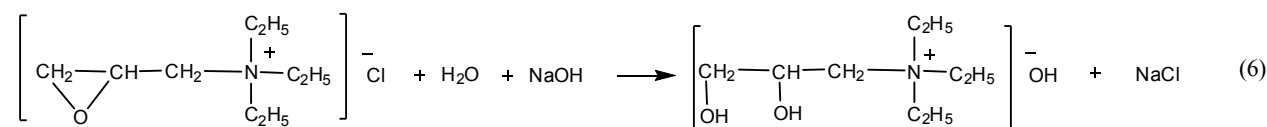
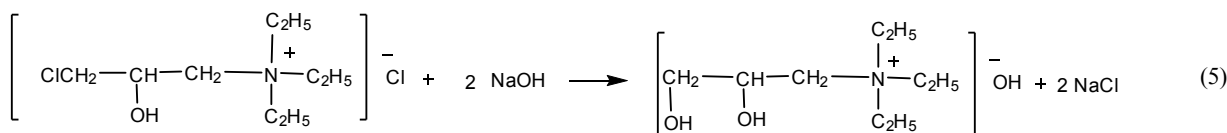
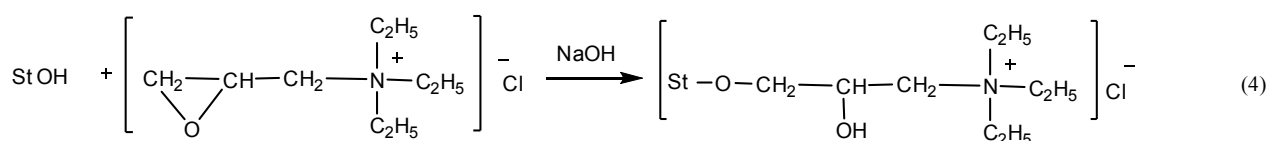
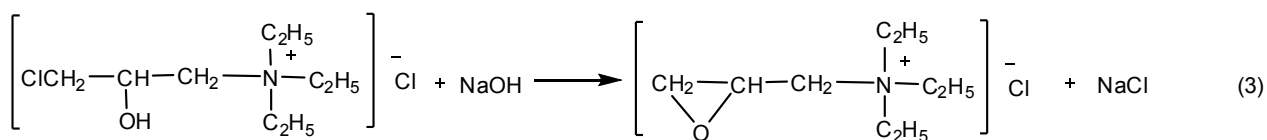
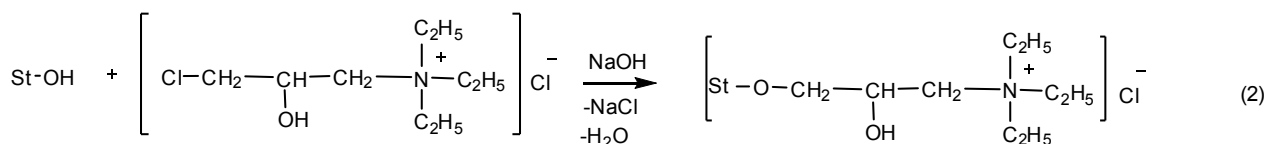
#### Results and discussion

The synthesis of the AR with a quaternary ammonium cation group occurs through the interaction of ECH with triethylammonium chloride (1).

The resulting AR is used to introduce the amino fragment into a starch macromolecule. The principal reaction of starch with the AR in the presence of NaOH may be illustrated as follows (2).

Sodium hydroxide in a certain relative amount to the AR acts as a catalyst and promotes the





formation of 3,4-epoxypropyltriethylammonium chloride (3) which forms an ether linkage with starch (4) [9].

Together with the principal reaction of a starch cationation, an excess of NaOH may cause the formation of a by-product, diol (5), (6).

The hydrolysis of the final product in an excess of sodium hydroxide may proceed according to the following scheme (7).

All reactions (5)–(7) reduce the effectiveness of a starch cationation.

#### IR spectroscopy

IR spectra of the AR, intact and the cationic starch were recorded to determine the structure of the cationic starch. The IR spectrum of the aminating reagent, 3-chloro-2-hydroxypropyltriethylammonium chloride, (Fig. 1) shows absorptions at 1472 and 1396  $\text{cm}^{-1}$  that can be assigned to vibrations of groups such as  $-\text{CH}_2-$  and  $-\text{CH}_3$ , which are present in the 2-hydroxypropyltriethylammonium chloride moiety. The similar vibrations appear in the spectrum of the cationic starch (Fig. 2), these are absent in intact starch.

The absorptions at 1308, 742 and 700  $\text{cm}^{-1}$  are attributed to  $-\text{CH}_2\text{-Cl}$  [11], the lack of these

absorptions in the spectrum of the purified cationic starch confirms the reaction of ether formation (2). The bands at 2930 and 2828  $\text{cm}^{-1}$  arise from the presence of  $-\text{CH}_2-$  groups along with 3320  $\text{cm}^{-1}$  from C–H vibrations. The absorptions at 1264 and 1089  $\text{cm}^{-1}$  are due to  $-\text{OH}$  secondary groups. The absorptions at 3480 and 3376  $\text{cm}^{-1}$  suggest the presence of  $-\text{OH}$  polyassociations (wide bands between 3400 and 3200  $\text{cm}^{-1}$ ) [11]. Vibrations that appear at 2110 and 1640  $\text{cm}^{-1}$  refer to  $-\text{OH}$  associations with water molecules remaining after drying.

The absorption at 930  $\text{cm}^{-1}$  in the spectrum of intact starch results from C–O–C oscillations of an  $\alpha$ -1,4-glycosidic linkage inherent in amylose and amylopectin molecules as well as an  $\alpha$ -1,6-glycosidic linkage in amylopectin ones [12,13]. Similar vibrations (i.e. at 940  $\text{cm}^{-1}$ ) are present in the St–O–AR spectrum showing the C–O–C stretching mode of a glycosidic linkage. It is important that the absorptions in the regions of 1200–950  $\text{cm}^{-1}$  and 1500–1200  $\text{cm}^{-1}$  in the spectrum of intact starch and in the spectrum of the St–O–AR (Fig. 2, A, B) are strongly overlapped; therefore a clear definition is complicated. The bands at 1150, 1089 and 1030  $\text{cm}^{-1}$

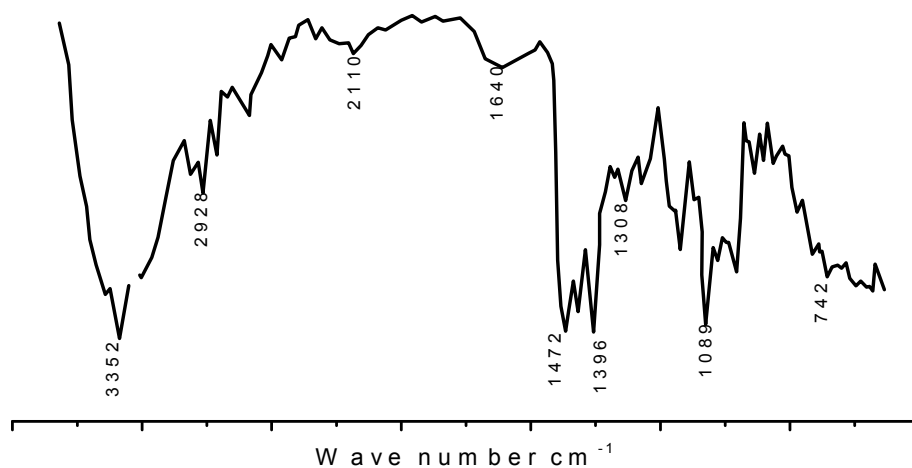


Fig. 1. The IR spectrum of the aminating reagent 3-chloro-2-hydroxypropyltriethylammonium chloride

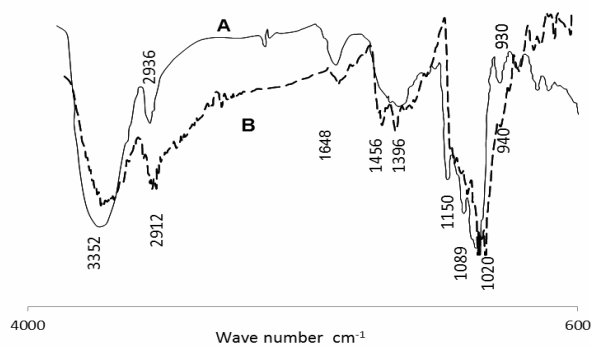


Fig. 2. The IR spectra of intact starch (curve A) and cationic starch (curve B)

in the spectrum of intact starch, in addition to the corresponding ones at 1150, 1080 and 1020  $\text{cm}^{-1}$  in the spectrum of the St-O-AR, are typical of the C-O vibrations. The absorptions at 1150, 1089  $\text{cm}^{-1}$  (Fig. 2, A) and 1150, 1080  $\text{cm}^{-1}$  (Fig. 2, B) suggest the presence of C-O-H. The absorption at 1020  $\text{cm}^{-1}$  in both spectra results from the O-C vibrations of the pyranose form [13,14].

At the same time, it is evident that the intensity of the bands at 1150  $\text{cm}^{-1}$  (the signal splits badly) and 1080  $\text{cm}^{-1}$  in the spectrum of the St-O-AR decrease when compared with those in the spectrum of intact starch. This can be used to substantiate the formation of ether linkages with the -2-hydroxypropyltriethylammonium chloride moiety.

The confirmation that the bonds are related to the  $-\text{CH}_2\text{OH}$  group originates from the badly split bands in the region of 1400 to 1300  $\text{cm}^{-1}$ , namely: 1450, 1412, 1365 and 1242  $\text{cm}^{-1}$ . Alterations occur in this region in the spectrum of the St-O-AR (1400 to 1300  $\text{cm}^{-1}$ ) after the modification of intact starch: the band broadens and more intense bands at 1456 and 1396  $\text{cm}^{-1}$  emerge due to both the methylene

scissoring and the methyl asymmetric bending modes which are present in the -2-hydroxypropyltriethylammonium chloride moiety [12]. Analogous bands are present in the spectrum of 3-chloro-2-hydroxypropyltriethylammonium chloride (Fig. 1) and absent in the spectrum of intact starch. The absorptions of even low intensity at 1643  $\text{cm}^{-1}$  in the spectrum of intact starch and 1648  $\text{cm}^{-1}$  in the spectrum of the St-O-AR suggest the affinity of the samples for water [12].

Both the spectra exhibit the broad absorption between 3400 and 3200  $\text{cm}^{-1}$  consistent with an O-H stretching mode due to intermolecular hydrogen bonding. Slight shifting and widening of this band in the spectrum of the St-O-AR (3352–3240  $\text{cm}^{-1}$ ) can be observed when compared with the spectrum of intact starch (3370  $\text{cm}^{-1}$ ). This is due to the deviations of the configuration by forming new hydrogen bonding and cleaving existent ones as well as the influence of adjacent functional groups. The absorption resulted from C-H stretching is seen at 2936  $\text{cm}^{-1}$  in the spectrum of intact starch. The respective absorption in the spectrum of the St-O-AR at 2936  $\text{cm}^{-1}$  is revealed in more wide and intense shape; it argues for new C-H in the -2-hydroxypropyltriethylammonium chloride moiety [7].

To estimate the interaction of the AR with corn starch in the presence of sodium hydroxide by the above mentioned semi-dry method, the following criteria were used: the degree of substitution of the replaced hydrogen atoms in the hydroxy groups of starches with amino containing fragments (i.e. the degree of cationation) with ether formation, and the effectiveness of this reaction. The dependences of the DS and the ER as functions of the relationships between the content of AR, NaOH and the D-glucopyranose unit (GU) were scrutinized at constant

temperatures and the duration of the reaction.

#### *Effect of sodium hydroxide*

Sodium hydroxide itself acts either as a catalyst in the reactions (2), (4), and (7) or as an initial reagent. Fig. 3 represents the plot of the DS vs. the NaOH:AR ratio in the starting reaction mixture at different ratio of the AR to the GU.

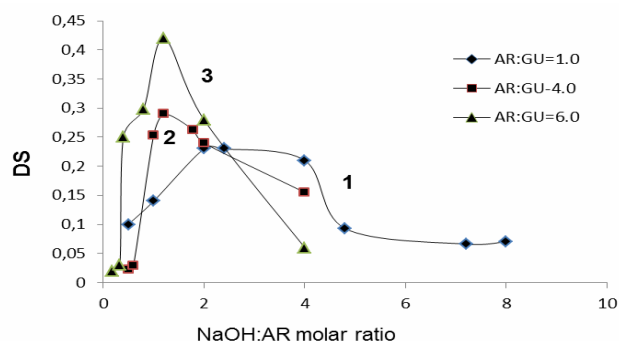


Fig. 3. The dependence of the DS on the NaOH:AR molar ratio in the starting reaction mixture at the different AR:GU molar ratios. The reaction conditions are as follows: duration of 7 hours and temperature of 40°C

It is evident from Fig. 3 that the DS appreciably depends upon the NaOH:AR ratio at any AR:GU ratio. When the NaOH:AR ratio is less than 1.2, the DS has a little value. As the NaOH:AR ratio increases, the DS increases and some optimal NaOH:AR ratio is observed. The optimal NaOH:AR ratio is within the range of 1.2 to 2.0 at almost each ratio of the AR to the GU. If the NaOH:AR ratio is higher than the optimal one, the DS decreases accordingly. This can be explained by the fact that an increase in the NaOH excess causes both an increase in the share of hydrolytic reactions (5), (6) and (7) and a decrease in the effectiveness of the starch cationation.

#### *Effect of the AR:GU molar ratio*

It is evident that an increase in the AR:GU ratio (within the investigated ratio range of 1.0 to 6.0) is accompanied by an increase in the DS. At the same time, it is important to note that the above mentioned relationship is especially pronounced at NaOH:AR=1.0 (when this ratio is less than the optimal value, 1.2): the DS increases from 0.14 to 0.35 (Table, Fig. 3).

At NaOH:AR=2.0 (more than the optimal value, 1.2), an increase in the DS is insignificant and practically constant, although the ratio AR:GU increases from 1.0 to 6.0 (Table, Fig. 3). At a further increase in the NaOH:AR ratio (NaOH:AR is more than 2.0), the DS decreases antiprobably to AR:GU

(Fig. 3).

#### **Dependence of the DS upon the initial AR:GU molar ratio\***

AR:GU, molar ratio	DS	
	NaOH:AR=1.0, molar ratio	NaOH:AR=2.0, molar ratio
1.0	0.14	0.23
2.0	0.20	0.22
4.0	0.25	0.24
6.0	0.35	0.30

\*Note: – The reaction conditions are as follows: duration of 7 hours and temperature of 40°C

It is clear (Fig. 4) that the most effective cationation proceeds at the lowest ratio AR:GU=1.0 (in the researched range of the AR:GU). This can be attributed to both the need for some NaOH excess in the reaction mixture and the steric peculiarities of the interaction between the starch and the AR.

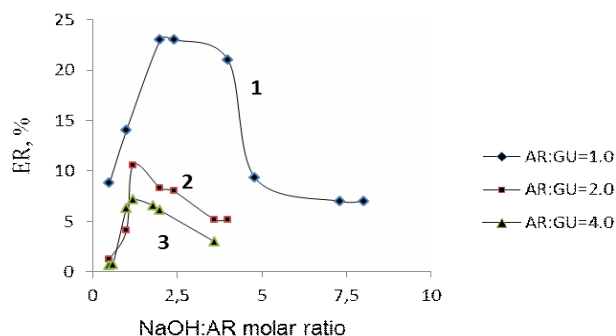


Fig. 4. The dependence of the ER on the NaOH:AR molar ratio

When performing the reaction by a semi-dry method, the interaction of the AR occurs on the surface of starch granules accompanied by the gradual diffusion of the reagent into underlying layers. It is known that starch contains two major fractions: linear amylose and branched amylopectin that, in turn, forms the amorphous-crystalline structure of starch granules [8,15]. It is considered that a starch cationation occurs mainly within half-packed amorphous areas, which branched from amylopectin forms [8]. These amylopectin chains are more sterically available. When the concentration of the AR is high at the first moment, the active interaction occurs with the hydroxy groups of the glucopyranose form. Subsequently, the amount of the accessible hydroxy groups decreases.

The -2-hydroxypropyltriethylammonium

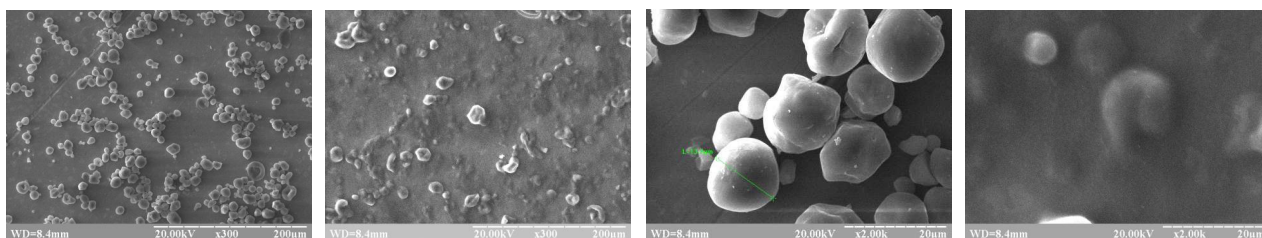


Fig. 5. SEM images of unmodified starch previously kept in distilled water at 40°C for 2 hours and the cationic starch samples in the reaction mixture at AR:GU=1.0 and NaOH:AR=1.2. The reaction duration is 2 hours

chloride fragments, which are connected to the glucopyranose cycles by ether linkages, create steric hindrance to further cationation [13]. Moreover, an increase in the NaOH amount leads to the hydrolysis of the final product (7) and to the side reactions (5) and (6).

Scanning electron microscopy was used to visualize the change in the starch granules and reactive media during cationation. Figure 5 (A and C) show the images of unmodified starch previously kept in distilled water at 4°C for 2 hours and the cationic starch in the reactive medium.

One can see that the intact corn starch granules are round and polygonal in shape with a good distinctive surface. In the course of the interaction with the AR, the starch granules lose their well-defined form; the granules diminish in their size, disintegrate and begin to dissolve (Fig. 5, B and D).

### Conclusions

1. The aminating reagent, 3-chloro-2-hydroxypropyltriethylammonium chloride, was prepared by the interaction of triethylammonium chloride with epichlorohydrin in the presence of cetyltrimethylammonium bromide as a catalyst.

2. In the course of the interaction of 3-chloro-2-hydroxypropyltriethylammonium chloride with corn starch via a semi-dry method in the presence of sodium hydroxide, the cationic starch was obtained with a degree of substitution equal to 0.02–0.35. It was shown that the cationic starch with the highest degree of substitution was fabricated when the NaOH:AR molar ratio in the starting reaction mixture was equal to 1.2–2.0.

3. The highest effectiveness of cationation was achieved when the AR and the GU were in 1:1 molar ratio in the starting reaction mixture.

### REFERENCES

- Zargar V., Asghari M., Dashti A. A review on chitin and chitosan polymers: structure, chemistry, solubility, derivatives, and applications // *ChemBioEng Rev.* – 2015. – Vol.2. – P.204-226.
- Kriazhev V.N., Romanov V.V., Shyrokov V.A. Poslednie dostizheniya khimii i tekhnologii proizvodnykh krakhmala // *Khimiya Rastitel'nogo Syr'ya.* – 2010. – No. 1. – P.5-12.
- Prado H.J., Matulewicz M.C. Cationization of polysaccharides: a path to greener derivatives with many industrial applications // *Eur. Polym. J.* – 2014. – Vol.52. – P.53-75.
- Cationic starch-enhanced ultrafiltration for Cr(VI) removal / Baek K., Yang J.-S., Kwon T.-S., Yang J.W. // *Desalination.* – 2007. – Vol.206. – P.245-250.
- Antibacterial activity and biocompatibility of a chitosan- $\gamma$ -poly(glutamic acid) polyelectrolyte complex hydrogel / Tsoo C.T., Chang C.H., Lin Y.Y., Wu M.F., Wang J.-L., Han J.L., Hsieh K.H. // *Carbohydr. Res.* – 2010. – Vol.345. – P.1774-1780.
- Ionically and covalently crosslinked hydrogel particles based on chitosan and poly(ethylene glycol) / Popadyuk N., Zholobko O., Donchak V., Harhay H., Budishevskaya O., Voronov A., Kohut A., Voronov S. // *Chem. Chem. Technol.* – 2014. – Vol.8. – No. 2. – P.171-176.
- Preparation and characterization of cationic corn starch with a high degree of substitution in dioxane-THF-water media / Wang P.-X., Wu X.-I., Dong-hua X., Kun X., Ying T., Xi-bing D., Wen-bo L. // *Carbohydr. Res.* – 2009. – Vol.344. – P.851-855.
- Litviak V.V., Kanarskii A.V. Osobennosti kationizatsii  $\alpha$ -D-glukoparanozy krakhmala v polozhenii 3C atoma (N-3-khloro-2-gidroksipropil)-N,N,N-trimetilammonii khloridom // *Plasticheskie Massy.* – 2016. – No. 7-8. – P.27-31.
- Khalil M.I., Farag S. Preparation of some cationic starches using the dry process // *Starch/Stärke.* – 1998. – Vol.50. – No. 6. – P.267-271.
- Cheronis N., Ma T.S. Mikro- i polumikro metody organicheskogo funktsional'nogo analiza. – M.: Khimiya, 1973. – 576 p.
- Kazitsyna L.A., Kupletskaya N.B. Primenenie UF-, IR- i YaMR-spektroskopii v organicheskoi khimii. – M.: Vysshaya shkola, 1971. – 264 p.
- Kizil R., Irudayaraj J., Seetharaman K. Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy // *J. Agric. Food Chem.* – 2002. – Vol.50. – P.3912-3918.
- The chemical modification of a range of starches under aqueous reaction conditions / J.M. Fang, P.A. Fowler, C. Sayers, P.A. Williams // *Carbohydr. Polym.* – 2004. – Vol.55. – P.283-289.
- Polymer-polymer miscibility in PEO/cationic starch

and PEO/hydrophobic starch blends / A.G.B. Pereira, A.T. Paulino, A.F. Rubira, E.C. Muniz // *eXPRESS Polym. Lett.* – 2010. – Vol.4. – No. 8. – P.488-499.

15. Liu Q., Li J., Xu W. Application of cationic starch with high degree of substitution in packaging paper from high yield pulp // *Proc. of the 17<sup>th</sup> IAPRI world conference on packaging (IAPRI 2010 PAPERBACK)*. – 2010. – P.35-38.

Received 22.04.2019

#### КАТІОНУВАННЯ КРОХМАЛІВ АМІНУЮЧИМ РЕАГЕНТОМ НА ОСНОВІ ТРИЕТИЛАМІНУ І ЕПІХЛОРОГІДРИНУ

О.А. Костик, О.Г. Будішевська, В.Б. Вострес,  
З.Я. Надашкевич, С.А. Воронов

У даній роботі спрощеним методом одержано катіонні крохмалі з різним ступенем заміщення з використанням триетиламіну та епіхлоргідрину як вихідних реагентів і досліджено і оптимізовано умови катіонування крохмалю «напівсухим методом». Катіонний крохмаль з четвертинними амонійними катіонними групами одержували взаємодією амінуючого реагенту з кукурудзяним крохмалем у присутності натрій гідроксиду. Амінуючий реагент 3-хлоро-2-гідроксипропілтриетиламоній хлорид одержано одnoreакторним методом взаємодією триетиламіну з хлоридною кислотою з наступною реакцією триетиламоній хлориду з епіхлоргідрином у присутності каталізатора триметилацетиламоній броміду. Взаємодією 3-хлоро-2-гідроксипропілтриетиламоній хлориду з кукурудзяним крохмалем у присутності натрій гідроксиду одержано катіонні крохмалі із ступенем заміщення атомів Гідрогену в гідроксильних групах крохмалю 0,02-0,45. Досліджено вплив мольного співвідношення натрій гідроксид:амінуючий реагент та співвідношення амінуючий реагент:крохмаль (ланки D-глюкопіранози) у вихідній реакційній суміші на ступінь заміщення. Показано, що катіонний крохмаль з найвищим ступенем заміщення утворюється при початковому оптимальному співвідношенні натрій гідроксид:амінуючий реагент, рівному 1,2–2,0. Збільшення співвідношення амінуючий реагент:крохмаль при вмісті натрій гідроксиду менше оптимального суттєво збільшує ступінь заміщення. Ефективність реакції катіонування кукурудзяного крохмалю зменшується при збільшенні мольного співвідношення амінуючий реагент:крохмаль (у досліджуваному інтервалі 1,0–6,0).

Ключові слова: катіонний крохмаль, амінуючий реагент, ступінь заміщення, триетиламін, епіхлоргідрин.

#### CATIONIZATION OF STARCH WITH AN AMINATING REAGENT BASED ON TRIETHYLAMINE AND EPICHLOROHYDRIN

О.А. Костык, О.Г. Будисhevskaya \*, В.Б. Вострес,  
З.Я. Надашкевич, С.А. Воронов

Lviv Polytechnic National University, Lviv, Ukraine

\* e-mail: budishevskaya@gmail.com

This article presents a simplified method for the preparation of cationic starches with a different degree of substitution using triethylamine and epichlorohydrin as starting materials. The optimal conditions for a starch cationization by a semi-dry method have been determined. The cationic starch with quaternary ammonium cation

groups was prepared by the interaction of an aminating reagent with corn starch in the presence of sodium hydroxide. The aminating reagent, 3-chloro-2-hydroxypropyltriethylammonium chloride, was synthesized by the one-pot interaction between triethylamine and HCl followed by the reaction with epichlorohydrin in the presence of cetyltrimethylammonium bromide as a catalyst. The cationic starches were fabricated with the degree of substitution of hydrogen atoms in starch hydroxy groups equal to 0.02–0.45. The effects of molar ratios of sodium hydroxide to the aminating reagent and the aminating reagent to starch (with respect to a D-glucopyranose unit) in the initial reaction mixture on the degree of substitution were investigated. It was shown that the cationic starch with the highest degree of substitution was formed at an optimal starting molar ratio of sodium hydroxide to the aminating reagent that is equal to 1.2–2.0. An increase in the molar ratio of aminating reagent to starch significantly increases the degree of substitution when the content of sodium hydroxide is less than the optimal value. The reaction efficiency of the cationation of corn starch decreases with an increase in the molar ratio of aminating reagent to starch (in the test range of 1.0 to 6.0).

**Keywords:** cationic starch; aminating reagent; degree of substitution; triethylamine; epichlorohydrin.

#### REFERENCES

- Zargar V., Asghari M., Dashti A. A review on chitin and chitosan polymers: structure, chemistry, solubility, derivatives, and applications. *ChemBioEng Reviews*, 2015, vol. 2, pp. 204-226.
- Kriazhev V.N., Romanov V.V., Shyrokov V.A. Poslednie dostizheniya khimii i tekhnologii proizvodnykh krakhmala [State-of-the-art of chemistry and technology of starch derivatives]. *Khimiya Rastitel'nogo Syr'ya*, 2010, no. 1, pp. 5-12. (in Russian).
- Prado H.J., Matulewicz M.C. Cationization of polysaccharides: a path to greener derivatives with many industrial applications. *European Polymer Journal*, 2014, vol. 52, pp. 53-75.
- Baek K., Yang J.-S., Kwon T.-S., Yang J.W. Cationic starch-enhanced ultrafiltration for Cr(VI) removal. *Desalination*, 2007, vol. 206, pp. 245-250.
- Tsao C.T., Chang C.H., Lin Y.Y., Wu M.F., Wang J.-L., Han J.L., Hsieh K.H. Antibacterial activity and biocompatibility of a chitosan- $\gamma$ -poly(glutamic acid) polyelectrolyte complex hydrogel. *Carbohydrate Research*, 2010, vol. 345, pp. 1774-1780.
- Popadyuk N., Zholobko O., Donchak V., Harhay K., Budishevskaya O., Voronov A., Kohut A., Voronov S. Ionically and covalently crosslinked hydrogel particles based on chitosan and poly(ethylene glycol). *Chemistry & Chemical Technology*, 2014, vol. 8, no. 2, pp. 171-176.
- Wang P.-X., Wu X.-I., Dong-hua X., Kun X., Ying T., Xi-bing D., Wen-bo L. Preparation and characterization of cationic corn starch with a high degree of substitution in dioxane-THF-water media. *Carbohydrate Research*, 2009, vol. 344, pp. 851-855.
- Litviak V.V., Kanarskii A.V. Osobennosti kationizatsii  $\alpha$ -D-glukopiranozy krakhmala v polozenii 3C atoma (N-3-khloro-2-gidroksipropil)-N,N,N-trimetilammonii khloridom [Features of the cationization of  $\alpha$ -D-glucopyranose starch in position 3C atom by (N-3-chloro-2-hydroxypropyl)-N,N,N-trimethylammonium chloride]. *Plasticheskie Massy*, 2016, no. 7-8, pp. 27-31. (in Russian).

9. Khalil M.I., Farag S. Preparation of some cationic starches using the dry process. *Starch/Stärke*, 1998, vol. 50, pp. 267-271.

10. Cheronis N., Ma T.S., *Mikro- i polumikrometody organicheskogo funktsionalnogo analiza* [Micro- and semi-micro methods of organic functional analysis]. Khimiya, Moscow, 1973. 576 p. (in Russian).

11. Kazitsyna L.A., Kupletskaia N.B., *Primenenie UF-, IK- I YaMR-spektroskopii v organicheskoi khimii* [UV, IR and NMR spectroscopy in organic chemistry]. Vysshaya Shkola, Moscow, 1971. 264 p. (in Russian).

12. Kizil R., Irudayaraj J., Seetharaman K. Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy. *Journal of Agricultural and Food Chemistry*, 2002, vol. 50, pp. 3912-3918.

13. Fang J.M., Fowler P.A., Sayers C., Williams P.A. The chemical modification of a range of starches under aqueous reaction conditions. *Carbohydrate Polymers*, 2004, vol. 55, pp. 283-289.

14. Pereira A.G.B., Paulino A.T., Rubira A.F., Muniz E.C. Polymer-polymer miscibility in PEO/cationic starch and PEO/hydrophobic starch blends. *eXPRESS Polymer Letters*, 2010, vol. 4, no. 8, pp. 488-499.

15. Liu Q., Li J., Xu W., Application of cationic starch with high degree of substitution in packaging paper from high yield pulp. *Proceedings of the 17th IAPRI World Conference on Packaging*, 2010, pp. 35-38.