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OBTAINING OF HYDROXYPROPYL STARCH DERIVATIVES AND THEIR PROPERTIES

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Starch ethers were obtained under various conditions, i.e. hydroxypropylammonium starch as cationic starch and hydroxypropyl starch. The degree of substitution of starch ethers and their properties were examined.

INTRODUCTION

Modified starches may be obtained by various methods, acting with physical and chemical factors. The main modified starches are esters and starch ethers and oxidation products. Starch ethers are produced by an introduction of alkyl radical instead of hydrogen in the alcohol group. Formation of these compounds is possible in polysaccharides, including starch, owing to the presence of hydroxyl groups in each glucose residue [3]. The physico-chemical properties of starch ethers depend on the type of the etherifying compound used, conditions of reaction and degree of substitution. Ethylene oxide, propylene oxide and other substances are used as etherifying agents [4]. The characteristic feature of the obtained is the so-called substitution degree, expressing the number of substituents per one glucose residue in starch [9]. Starch ethers with a low degree of substitution have a substitution degree to value 1 at the utmost. They are generally water-soluble. The increase the density of paper and are suitable for surface sizing and coating of thin smooth paper like that used e.g. for illustrations. In case of obtaining hydroxypropyl

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ether of starch (Fig. 1) by the action of propylene oxide on starch, it is added in an amount of 1-25% of the dry substance of starch [12].

Hydroxypropyl ethers of oxidized starch reveal a lowered viscosity of pastes. They find also application in the paper-making industry [10].

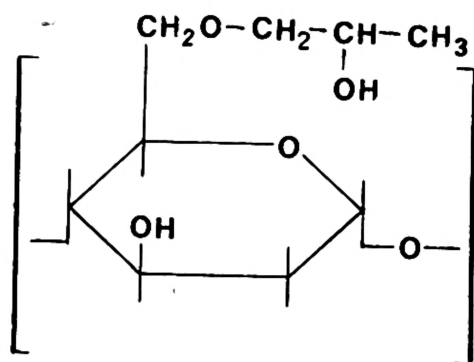


Fig. 1. Hydroxypropyl starch (fragment)

Starch ethers with a high degree of substitution show a substitution degree of 2-3. They are not soluble in water, only in organic solvents. The highly substituted starch ethers such as e.g. hydroxypropyl ether of starch have thermoplastic properties. After mixing with plasticizers, packaging foils may be obtained [13].

Starch ether derivatives are cationic electro-positive starches, formed by an introduction of the tertiary amino- or quaternary ammonium group to starch as, for example, in the case of hydroxypropylammonium starch [2, 8] (Fig. 2). The etherifying agent here is 3-chloro-2-hydroxypropyl-trimethyl-ammonium chloride (Fig. 3), called "Quab" preparation [1].

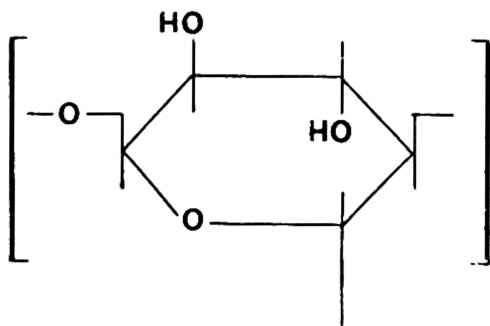


Fig. 2. Trimethyl-2-hydroxypropyl-ammonium starch (cationic starch — fragment)

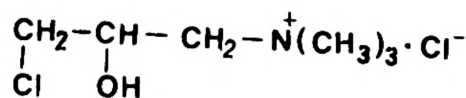


Fig. 3. 3-chloro-2-hydroxypropyl-trimethyl-ammonium chloride

Cationic starches find application, among other things, as flocculants for the coagulation of sediments, e.g. in wastes treatment but first of all, in the paper-making industry for increasing paper strength and improvement of paper surface [5].

The purpose of the conducted experiments was to examine the influence of the conditions of reaction on the obtained degree of substitution and properties of the obtained starch ethers, i.e. preparations of hydroxypropylammonium and hydroxypropyl starch and products of its oxidation.

EXPERIMENTAL

METHODS OF THE EXPERIMENT

In the obtained preparations of modified starches, the following determinations were made:

- humidity by drying at 125°C (398 K);
- pH, with the use of a pH-meter with glass electrode produced by the Radiometer company,
- viscosity of 5% pastes, using a rotary viscosimeter produced by Contraves,
- ash content by torrefaction at 600°C (873 K),
- degree of etherification of cationic starch, i.e. number of hydroxypropyl-ammonium groups (HPA) for 1 glucose residue (G); determining the equivalent amount of nitrogen by Kjeldahl method;
- cationity of etherified starch on the basis of the capacity of binding with kaolin and acceleration of its sedimentation in water suspension (1000 cm³ suspension, 0.1% English kaolin and 10 cm³ 0.1% solution of preparation of hydroxypropyl-ammonium starch); cationity of the preparation is expressed in volume of kaolin subjected to sedimentation during 12 minutes;
- % solubility in water at various temperatures during 30 minutes, measurements with the use of immersion refractometer at 20°C (293 K);
- degree of substitution of hydroxypropyl starch, i.e. number of hydroxypropyl (HP) groups for 1 glucose residue (G):
 - a) by the methods of Lortz [6] and Morgan [7] by distillation with hydriodic acid and determinations of the quantity of the produced propyl iodide and propylene being made their sum is equivalent to the number of hydroxypropyl groups in starch,
 - b) by the method of Stahl and McNaught [11] applying nuclear magnetic resonance (NMR); for this purpose, the sample of hydroxypropyl starch is hydrolysed with hydrochloric acid and the solution of acetic acid as an internal standard, is introduced to an NMR tube and inserted to spectrophotometer (type 487 C, Tesla); from the obtained spectrum, i.e. integration of peaks, the results of measurements are obtained,
- the effectiveness of reaction of starch etherification, i.e. substitution with hydroxypropyl groups was calculated in % of the more expensive component, i.e. the quantity of propylene oxide, chemically linked by starch in relation to the total amount of propylene oxide introduced to the reaction.

THE EXPERIMENT

In the first series of the experiments, hydroxypropyl-ammonium starch was obtained by action of "Quab" preparation at 35°C (308 K) for 8 h, on the suspension of starch in water, alkalized with the addition of calcium hydroxide. Ratio of the components: 990 cm³ water, 900 g potato flour, humidity 20%, 330 cm³ of 3% Ca(OH)₂ added in two doses; 27 cm³ of "Quab" preparation. After the completion of the etherification reaction, part of the sample was filtrated directly on glass filter and rinsed with water and part of the sample before filtration was neutralized with sulphuric acid. The filtrated samples of etherified starch were dried in

Table 1. Composition and properties of preparations of hydroxypropyl-ammonium starch (HPA starch) obtained under different conditions. (Suspension of starch in water alkalized with Ca(OH)₂ with the addition of "Quab" preparation; time of preliminary reaction 8 hours at 35°C)

Conditions of the process of obtaining starch ether		Trimethyl-hydroxypropyl-ammonium starch				
Treatment after preliminary reaction	drying at 100°C	ash content (%)	5% paste at 20°C		degree of substitution HPA/1G	cationity (sedimentation volume of kaolin, cm ³)
			pH	viscosity (mPa · s)		
Rinsing with water	in dryer with air flow	0.528	9.7	gel	0.013	1.0
	in roller dryer	0.643	9.1	341.7	0.017	1.4
	in roller dryer with the addition of Na ₂ B ₄ O ₇ · 10H ₂ O, Al ₂ (SO ₄) ₃ , NaHSO ₄	2.102	3.9	485.1	0.018	1.6
Neutralization with the use of H ₂ SO ₄	in dryer with air flow	0.109	6.85	gel	0.022	1.6
	in roller dryer	0.371	6.75	1155	0.030	8.1
	in roller dryer with the addition of Na ₂ B ₄ O ₇ · 10H ₂ O, Al ₂ (SO ₄) ₃ , NaHSO ₄	2.155	2.9	24.0	0.043	9.0

a dryer with air flow at a gradually increased temperature from 70 to 100°C (343-373 K) or after mixing with water dried in a roller dryer. One more variant was introduced in which borax, aluminium sulphate and sodium bisulphate (for 2250 cm³ water — 1.8 g of Na₂B₄O₇·10 H₂O; 7.2 g of Al₂(SO₄)₃; 18 g NaHSO₄) were added to water before mixing with etherified starch and then the suspension was dried in a roller dryer.

During the reaction of starch with "Quab" preparation, the rate of substitution reaction was monitored. For this purpose, the samples were taken at the beginning of the reaction and then every 2 hours; the samples were filtrated, rinsed with water and dried, then the percentage of water and nitrogen was determined. The results of the experiments are presented in Tables 1, 2 and 3.

Table 2. Solubility of hydroxypropyl-ammonium starch depending on water temperature during dissolution

Cationity, volume of sedimentation kaolin, cm ³	Solubility of starch ether at temperature		
	20°C	40°C	80°C
9.0	83%	97%	99%

Table 3. Increment of substitution degree of hydroxypropylammonium starch (HPA starch) depending on reaction time (etherification of starch in water suspension with the use of "Quab" preparation)

Time of reaction at 35°C (hours)	Degree of substitution of etherified starch (HPA groups per 1 G residue)
0.25	0.0038
2	0.0039
4	0.0047
6	0.0087
8	0.0260

In the second series of the experiments, hydroxypropyl starch was obtained by the etherification of starch with the use of propylene oxide in water solution at 38°C (311 K) during 72 h with continuous stirring. In order to avoid formation of starch paste sodium sulphate was added as an inhibitor in alkaline slurry. Proportions of the components: 100 cm³ water, 40 g Na₂SO₄; 1.5 g NaOH; 100 g potato starch with 20% humidity and 15 g propylene oxide. Every twelve hours or so, the samples were taken, neutralized, filtrated, rinsed and dried at 50-70°C (323-343 K), in a dryer with air flow. In the samples, water content and degree of substitution were determined. In the last sample, a complete analysis was performed (Table 4).

In the third series of experiments, the etherification of starch with the use of propylene oxide by the dry method under pressure, was

Table 4. Etherification of starch in water suspension with the use of propylene oxide (reaction of substitution with hydroxypropyl (HP) groups, at 38°C)

Time of reaction /hours)	Hydroxypropyl starch			
	ash content (%)	5% paste at 20°C		degree of substitution (HP groups) 1 g residue)
		pH	viscosity (mPa. s)	
1				0.018
22				0.044
46				0.059
72	0.340	6.5	10 620	0.066

conducted. For this purpose, to starch milk with a 36.5% concentration, 1-1.5% of disodium phosphate as catalyst in terms of dry matter was added, mixed, filtrated and dried at a temperature gradually increased to 50°C (323 K) to a water content, of about 10%. Slightly dried starch with phosphate was transferred to a pressure reactor and propylene oxide was added in various quantities from 1 to 20%, expressed in dry matter of starch. After blowing through the reactor with a neutral gas, i.e. nitrogen and after closing, the reaction of etherification during 8 h at 82°C (355 K) was conducted. During the first two hours of heating, pressure in the reactor was increased to 2 at then it was slowly lowered to 0 at.

The obtained preparations of hydroxypropyl starch were rinsed by mixing them twice, with ethanol and water solution (0.3:1) and filtrated. Starch preparations were dried in a dryer with air flow at 50-70°C (323-343 K) and analysed. The results of starch etherification with propylene oxide by the dry method are presented in Table 5.

Table 5. Characteristics and properties of hydroxypropyl starch preparations obtained by the dry method, depending in the quantity of propylene oxide used (time of reaction 8 h at 82°C)

Quantity of propylene oxide added (% per dry matter of starch)	Obtained hydroxypropyl starch					Yield of etherification (% of propylene oxide bound as compared with the introduced one)
	ash content (%)	5% paste at 20°C		propylene oxide bonded with starch (%)	degree of substitution (HP groups per 1 G residue)	
		Hp	viscosity (mPa. s)			
1	0.385	7.25	2 123	0.75	0.021	75.0
2.5	0.370	7.2	3 225	1.69	0.048	67.6
5	0.352	7.1	19 583	2.85	0.082	57.0
10	0.331	7.3	3 481	5.35	0.158	53.5
15	0.325	7.2	4 232	7 59	0.229	50.6
20	0.312	7.2	6 128	9.73	0.301	48.8

In the last experiments, etherification of starch with the use of propylene oxide was conducted in a water solution at 30°C (303 K) for 53 h with constant stirring. Due to the lower alkalinity of the environment in comparison with the second series of experiments, it was possible to decrease the dose of sodium sulphate as inhibitor of starch paste formation. Proportions of the components: 200 cm³ water, 0.65 g NaOH, 9.6 g Na₂SO₄, added in two parts; 120 g potato starch with 20% humidity and 24 g propylene oxide. After completion of the reaction, the pH value was lowered to about 6.5 with the use of hydrochloric acid and in order to oxidize the produced hydropropyl starch, sodium hypochlorite was introduced in quantities corresponding to: 1) 2 g of active chlorine; 2) 3 g of active chlorine/100 g of dry matter of starch what increased alkalinity of the solution; therefore, the pH value was lowered to 9, using hydrochloric acid. After 16 h of oxidation at 30°C (303 K), pH was lowered to ca 6.5 and the obtained product was rinsed by decantation and after filtration, it was dried at 35°C (308 K) in a dryer with air flow. The obtained products were analysed.

The results of the experiments of etherification and oxidation are shown in Table 6.

Table 6. Characteristics and properties of preparations of hydroxypropyl starch, oxidized with hydrochlorite, depending on the oxidizing agent used (etherification of starch with propylene oxide in water suspension at 30°C during 53 h; reaction of oxidation at 30°C during 16 h)

Quantity of active chlorine (% per d.m. of starch)	Oxidized hydroxypropyl starch					Yield of etherification (% of propylene oxide bound as compared to the introduced one)
	5% paste at 20°C		ash content (%)	propylene oxide bound with starch (%)	degree of substitution (HP groups per 1 G)	
	pH	viscosity (mPa · s)				
2	6.15	9.4	0.217	3.45	0.100	13.8
3	6.7	4.1	0.251	3.25	0.094	13.0

DISCUSSION OF THE RESULTS

The results obtained in the experiments show that when obtaining hydroxypropyl-ammonium starch (Table 1), the degree of substitution with HPA groups for 1 glucose residue (G) and cationity of the obtained preparation depend only slightly on the addition of various salts (borax, aluminium sulphate, sodium bisulphate) and to a higher degree, on the neutralization of the preparation's suspension in water, with the use of sulphuric acid. The greatest influence on the degree of substitution and

cationity was exerted by the method of drying the preparations. The roller dryer proved very useful in this respect. The obtained cationity of starch is good and its solubility in water is satisfactory (Table 2). It results from the experiments that drying of hydroxypropyl-ammonium starch in an increased temperature is a continuation of the etherification reaction. It is characteristic that the rate of substitution of starch with hydroxypropylammonium groups in a water suspension increased with the time of the reaction (during the 8 hours of the examination) which is shown in Table 3.

During the obtaining of hydroxypropyl starch, the rate of the process of starch etherification in water suspension was decreased gradually with the time of reaction (Table 4). This process, conducted for 72 h at 38°C (311 K) in starch milk gave a several times lower degree of substitution (0.066 HP groups/1 G residue) than the obtained 0.301 HP groups for 1 G residue, under the dry action of propylene oxide on potato starch under pressure at 82°C (355 K) during 8 h (Table 5). The dry course of the etherification process allows to apply a higher temperature of reaction without any hazard of starch glueing. When increasing the propylene oxide dose from 1 to 20% for dry matter of starch, a 15-fold increase of the substitution degree took place and the yield, expressed in propylene oxide, was lowered only 1.5 times.

The dry method of obtaining hydroxypropyl starch is thus definitely better especially as the time of reaction is 9-times shorter.

Hydrochloride oxidation of hydroxypropyl starch, obtained in water suspension (Table 6), caused a very considerable drop in the viscosity of 5% pastes from 10620 mPa.s (Table 4) 9.4 or 4.1 mPa.s (Table 6) depending on the dose of the oxidizing agent (2-3% of active Cl₂ for dry matter of starch) and the degree of substitution with hydroxypropyl groups depended to a small extent only on the dose of hydrochlorite.

CONCLUSIONS

The conducted experiments allow to draw the following conclusions:

1. The degree of substitution of hydroxypropyl-ammonium starch and its cationity increase during neutralization of post-reaction suspension with sulphuric acid.

2. Drying of hydroxypropyl-ammonium at an elevated temperature (100°C) is a continuation of the process of starch etherification; in particular, the degree of substitution, cationity and solubility in water are favourably increased in a roller dryer.

3. During obtaining hydroxypropyl starch by the "dry" method of etherification with the use of propylene oxide, under the pressure at 82°C,

a several-times higher degree of substitution of starch is reached and in a considerably shorter time than when the reaction is conducted in a water suspension of starch.

4. An increase of the dose of propylene oxide causes a proportional increase of the degree of substitution of starch with hydroxypropyl groups.

5. Oxidation of hydroxypropyl starch with the use of hypochlorite causes a many fold lowering in the viscosity of its pastes.

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OTRZYMYWANIE I WŁAŚCIWOŚCI POCHODNYCH SKROBI HYDROKSYPROPYLOWEJ

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Streszczenie

W przeprowadzanych doświadczeniach poddawano zawiesinę skrobi ziemniaczanej w wodzie w obecności wodorotlenku wapniowego w temp. 35°C w czasie 8 godz. działaniu chlorku trójmetylo-chlorohydroksypropylo-amoniowego. Uzyskaną skrobię hydroksypropyloamoniową poddawano działaniu różnych chemikaliów i suszeniu

w suszarce walcowej (najlepsze rezultaty) lub suszarce z przepływem powietrza (tab. 1). Oznaczono wpływ czasu reakcji na stopień podstawienia skrobi grupami hydroksypropyloamoniowymi (tab. 3) oraz wpływ obróbki chemikaliami podstawionej skrobi na lepkość jej kleików i kationowość (tab. 3).

W dalszych doświadczeniach poddawano skrobię ziemniaczaną z dodatkiem fosforanu dwusodowego jako katalizatora w stanie powietrznie suchym (zaw. ok. 10% wody) pod ciśnieniem działaniu tlenku propylenu w ilości 1-20% licząc na s.s. skrobi w czasie 8 godz. w temp. 82°C. Stopień podstawienia preparatów skrobi hydroksypropylowej oznaczano zarówno metodą Lortza z kwasem jodowodorowym, jak i za pomocą jądrowego magnetycznego rezonansu (NMR). Uzyskano interesujące wyniki wprost proporcjonalnej zależności stopnia eteryfikacji skrobi oraz zmiennej zależności lepkości kleików preparatów skrobi hydroksypropylowej od ilości użytego tlenku propylenu (tab. 5).

W końcowych doświadczeniach na zawiesinę skrobi działano w alkalicznym roztworze wodnym tlenkiem propylenu w temp. 38°C w ciągu 72 godz. oznaczając wpływ czasu reakcji na stopień eteryfikacji skrobi (tab. 4). Badano również wpływ utleniania podchlorynem na lepkość kleików skrobi hydroksypropylowej w zależności od dawki czynnego chloru, stwierdzając wielokrotne zmniejszenie lepkości.