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OBTAINING OF UREA-MODIFIED STARCHES AND THEIR PROPERTIES

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Key word: urea-modified starch

Starch was modified with the use of urea in presences of magnesium sulphate and sulphuric acid or phosphoric acid. The influence of various factors on the physico-chemical properties of modified starch was examined.

Starches modified with the use of urea give compounds which are not yet well recognized and are the products of the cross-linking of starch with the use of urea, either through condensation reactions of amino groups of urea with a carbonyl group of anomeric carbon of starch (C_1) or by the probable replacement of alcohol groups of starch (e.g. at carbons C_6) with the amino groups of urea. There are also amino sugars produced in a different way [2, 9]. It is also known that the use of diethylurea makes it possible to obtain starch ether [3, 7]. Depending on the conditions of reaction of starch modification with urea and accompanying chemical compounds, products with various properties may be obtained.

For example, the presence of phosphoric acid or phosphates at higher temperature may cause the formation of phosphate bonds in starch because it is well known that starch together with orthophosphoric acid produces (at C_6 carbons) ester, called amylophosphoric acid [2]. Starches modified with the use of urea play an important role as binders and glues in the chemical and paper-making industries.

The aim of the studies was to examine the influence of various physical and chemical factors on the properties of the obtained preparations of starch modified with urea.

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EXPERIMENTAL

Potato starch with a 20% water content was added to water solution at 50°C (323 K) containing magnesium sulphate, urea and sulphuric acid and it was mixed for 20 min. at 30°C (303 K). The mixture was dried at a temperature which was gradually raised from 50° to 90° (323-363 K) and after comminution of the semi-product, it was roasted at 125° (398 K). In the particular series of the experiment, the parameters of the process were successively changed, i.e. time of roasting, dose of sulphuric acid added, amount of urea and addition of magnesium sulphate. In the last experiments, magnesium sulphate was replaced with other salts and phosphoric acid was used instead of sulphuric acid.

The obtained preparations of urea-modified starch were analysed for the following determinations:

- water content by drying at 125°C (398 K) during 1.5 h [1, 5],
- viscosity of 20% pastes made by heating in water at 90°C (363 K) measured at 20°C (293 K) with the use of the rotary viscosimeter Contraves,
- reductivity by the Schoorl method, in % glucose [4, 5],
- brightness in a powdered state in comparison with permanent white barium carbonate (100%) with the use of Ulbricht ball [6].

RESULTS AND DISCUSSION

The results obtained in the first series of the experiments (Table 1) show that with the prolongation of the time of the main reaction, i.e. roasting at 125°C (398 K) for 1-7 hours, as a result of the processes taking place and first of all, due to the gradual diminution of free basic amino groups of urea subjected to binding with starch, pH value was distinctly lowered from 6.6 to 5.3 and the reductivity of the product was increased which points to the thermal degradation of starch and liberation of carbonyl groups at carbon C₁. However the increase of reductivity takes place maximum value of 0.669% was reached, the reductivity was again gradually lowered which was accompanied by a small increase in pH in the next hours of roasting. The decrease of reductivity is an evidence of the occurring increase of molecules of modified starch as a result of cross-linking with urea. This was confirmed by the determination of viscosity of 20% pastes. During the first hours of roasting, viscosity was lowered due to starch degradation processes and then there was an increase as a result of cross-linking. The brightness of the preparations with a prolonged time of roasting diminishes and their colour changes from white to more and more yellow.

The results of the second series of the experiments (Table 2) are fairly characteristic. The increase of the dose of sulphuric acid, causing a drop

Table 1. Influence of roasting time of potato meal with chemicals on the physico-chemical properties of urea-modified starch (for 100 g of meal — 25 cm³ water, 0.8 g MgSO₄ · 7H₂O, 10 g urea, 0.9 cm³ 96.6% H₂SO₄)

Time of roasting at 125°C (hours)	20% paste at 20°C		Reductivity, %	Modified starch	
	pH	viscosity (mPa · s)		brightness (% of permanent white barium carbonate)	colour
1	6.6	306	0.192	89	white
2	6.5	116	0.216	78	white-creamy
3	6.45	96.5	0.240	76	light-creamy
4	6.35	92	0.262	73.5	creamy
5	6.2	89.5	0.287	72	creamy
6	6.1	68.5	0.350	70.5	creamy
7	5.3	29.5	0.669	69	dark creamy
8	5.35	36.5	0.620	68	dark creamy
9	5.5	48.5	0.482	65	dark creamy
10	5.6	56.5	0.458	64	dark creamy

Table 2. Influence of the quantity of sulphuric acid on the physico-chemical properties of urea modified starch (or 100 g of meal — 25 cm³ water, 0.8 g MgSO₄ · 7H₂O, 10 g urea, roasting for 4 hours at 125°C)

Dose of 95.6% H ₂ SO ₄ (cm ³)	20% paste at 20°C		Reductivity (%)	Modified starch	
	pH	viscosity (mPa · s)		brightness (% of permanent white barium carbonate)	colour
0.1	—		0.077	96	white
0.2	6.95	565	0.093	94	white
0.4	6.9	123	0.133	92	white
0.6	6.7	99.5	0.167	84	white-creamy
0.8	6.4	95	0.229	79.5	white-creamy
1.0	6.3	80.5	0.282	73	creamy
1.2	6.2	39.8	0.363	70	creamy
1.4	6.15	98.3	0.490	65	dark-creamy
1.6	6.05	175	0.600	59	yellow
1.8	5.9	315	0.617	52	dark-yellow
2.0	5.85	445	0.693	46	brown-yellow

of the pH value, is accompanied by a permanent increase in reductivity of preparations of modified starch. This points to a release of new carbonyl groups at carbon C₁. Viscosity of 20% pastes however drops, to the level of sulphuric acid amounting to 1.2 cm³ only. When the addition of acid is further increased, viscosity of pastes is again increased in spite of

raising reductivity. This can well point to the occurring reactions of cross-linking of starch with cross bonds (e.g. at carbons C₆). The colour of modified starch preparations darkens further when the dose of sulphuric acid is increased.

Similar but reverse phenomena as in the experiments of the second series, were observed in the experiments of the third series (Table 3). The

Table 3. Influence of the quantity of urea on the physico-chemical properties of modified starch (for 100 g meal — 25 cm³ water, 0.8 g MgSO₄ · 7H₂O, 0.9 cm³ 95.6% H₂SO₄, roasting for 4 hours at 125°C)

Dose of urea (g)	20% paste at 20°C		Reductivity (%)	Modified starch	
	pH	viscosity (mPa · s)		brightness (% of permanent white barium carbonate)	colour
2	5.2	193.8	0.384	35.5	brown-grey
4	5.6	176	0.352	55	brown
6	5.85	156.5	0.335	60	yellow-brown
8	6.1	109	0.312	66	yellow
10	6.35	89.5	0.270	73.5	light-yellow
12	6.4	95	0.221	81	creamy
14	6.5	107	0.184	84	light-creamy
16	6.55	135	0.148	81	light-creamy
18	6.65	251	0.110	73.5	creamy
20	6.7	424	0.103	66.5	yellow

increasing doses of urea, possessing basic amino groups, cause a constant increase in pH and a lowering of reductivity of modified starch preparations. Viscosity of 20% pastes which was initially high (at smaller doses of urea) in spite of higher reductivity (domination of sulphuric acid in the environment) would point to a cross-linkage of starch with cross-bonds (at carbons C₆). Viscosity of pastes, however, is lowered with the increase of urea dose and then, starting from the level of 12 g of urea it rises again in accordance with the drop in reductivity of the preparations. This is an evidence of the cross-linking of starch with urea, from this moment on, also with the participation of bonds with carbon C₁. The colour of dry preparations of modified starches loses its intensity (the brightness of products increases) together with the rise of urea's quantity.

The results of the fourth series of the experiments demonstrate that an increase of the dose of sour salt i.e. magnesium sulphate causes a small lowering of the pH value of the environment and a permanent increase of reductivity in preparations of urea-modified starch (Table 4). Viscosity of 20% pastes of the preparations which initially decreased (to 80 mPa.s at dose of 1.0 g MgSO₄ · 7 H₂O) according to the progressive degradation of

Table 4. Influence of the level of magnesium sulphate added upon the physicochemical properties of urea-modified starches (for 100 g meal — 25 cm³ water, 10 g urea, 0.9 g 96.5% H₂SO₄, roasting for 4 hours at 125°C)

Dose of MgSO ₄ · 7H ₂ O (g)	20% paste at 20°C		Reductivity (%)	Modified starch	
	pH	viscosity (mPa · S)		brightness (% of permanent white barium carbonate)	colour
0.1	6.55	780	0.163	61.5	yellow
0.2	6.5	425	0.170	68	pale-yellow
0.4	6.45	255	0.180	70.5	pale-yellow
0.6	6.4	154	0.209	72	pale-yellow
0.8	6.35	91.5	0.260	73.5	pale-yellow
1.0	6.35	80	0.270	74	creamy
1.2	6.35	128	0.275	74.5	creamy
1.4	6.35	169	0.280	75	pale-creamy
1.6	6.35	180	0.284	75.5	pale-creamy
1.8	6.3	230	0.286	76	pale-creamy
2.0	6.3	292	0.291	77	pale-creamy
2.4	6.25	315	0.300	78.5	white-creamy
2.6	6.25	363	0.305	79	white-creamy
3.0	6.2	391	0.310	83	white-creamy

starch, afterwards increased (to 391 mPa.s) which would indicate that an increase in the dose of magnesium sulphate (from 1.2 g up) has a catalysing effect upon the cross-linking of starch with urea, with the help of cross bonds (e.g. at carbons C₆), a fact which takes place irrespectively of the increasing reductivity (increase of carbonyl groups at carbon C₁). An increase in the dose of magnesium sulphate, is accompanied by a growing brightness of modified starch preparation.

The fifth series of experiments was comparison of the action of various salts on the process of starch modification with urea. The results (Table 5)

Table 5. Influence of the type of salt added upon the physico-chemical properties of urea-modified starch. (for 100 g meal — 25 cm³ water, 0.8 g of various types of salt*), 10 g urea, 0.9 cm³ 95.6% H₂SO₄, roasting for 4 h at 125°C)

Type of salt	20% paste at 20°C		Reductivity (%)	Modified starch	
	pH	viscosity (mPa · s)		brightness (% of permanent white barium carbonate)	colour
MgSO ₄	6.35	190.5	0.285	75	creamy
NaCl	6.45	41	0.330	70	creamy
CaCl ₂	6.35	40	0.300	70	creamy
NH ₄ CNS	6.7	45.5	0.140	69	creamy

*) in dry matter

show that on case of 3 salts, i.e. magnesium sulphate, sodium chloride and calcium chloride, their influence on the reductivity of urea-modified starch products, i.e. on degradation of starch by sulphuric acid, was small. The reductivity of the product was distinctly lowered only by the addition of ammonium rhodanate, probably by increasing the pH value of the environment. Differences in colour and brightness of the obtained preparations of urea-modified starch were minimal, which means that the influence of the type of salt added was almost unnoticeable. On the other hand, viscosity of 20% pastes of modified starch in case of an addition of magnesium sulphate, was twice higher than in case of other salts, i.e. sodium chloride, ammonium rhodanate and calcium chloride. This shows that magnesium sulphate is more active and to a certain degree, it catalyses cross-linking of starch with urea.

In the sixth series of experiments, the influence of the level of phosphoric acid on the modification of starch with urea was examined; the doses of the remaining components were changed. An increase of the dose of 85% orthophosphoric acid from 1 to 5 cm³ (for 100 g meal) was reflected in a lowering of the pH value and an increase of reductivity of the obtained preparations whose brightness was smaller and smaller (Table 6). It is characteristic that the viscosities of pastes were high.

Table 6. Influence of the level of orthophosphoric acid on the physico-chemical properties of urea-modified starch (for 100 g meal — 25 cm³ water, 2 g MgSO₄ · 7H₂O, 12 g urea, roasting for 4 hours at 125°C)

Dose of 85% H ₃ PO ₄ (cm ³)	20% paste at 20°C		Reductivity (%)	Modified starch	
	pH	viscosity (mPa · s)		brightness (% per- manent white barium carbonate)	colour
1	7.2	630.0	0.115	75.2	pale-creamy
2	7.05	2540	0.122	78.5	pale-creamy
2.5	7.0	3844	0.125	80.7	pale-creamy
3	6.8	1732	0.128	72.3	pale-creamy
3.5	6.4	610.0	0.136	70.8	creamy
4	6.1	321.0	0.140	69.5	light-yellow
5	5.9	102.0	0.149	64.6	light-yellow

Viscosity of 20% pastes of modified starch reaches its maximum at a dose of 2.5 cm³ of phosphoric acid in spite of increased reductivity, that is release of carbonyl groups at carbon C₁.

There probably occurs a cross-linking of starches with the help of cross bonds (at carbons C₆) and the participation of urea as well as of phosphoric acid residues in these bonds is possible. This phenomenon

occurred especially at pH 7. When the pH value was further lowered, degradation of starch dominated and viscosity of pastes was again decreased.

CONCLUSIONS

Summing up the results of studies on the modification of starch with urea, it may be stated that this process is very complicated as in principle all the factors examined exerted their influence upon the changes occurring in starch. As a result of a repeated selection of the factors discussed, using a properly decreased dose of magnesium sulphate and increased level of sulphuric acid ratio (1:4) and shortening the roasting process carried out by the continuous method, a preparation of the so-called aminodextrin bearing the trade name of "Deksgum" was obtained. The preparation was patented [8] and introduced into production. This urea-modified starch preparation is characterized by a very high stability of pastes and capacity of easy rehydration; in connection with this fact, it may be used for the mechanical coating of paper (Scotch tapes, stamps, etc.). It may be also used as a glue or a binder for the purposes.

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OTRZYMYWANIE I WŁAŚCIWOŚCI SKROBI MODYFIKOWANYCH Z UDZIAŁEM MOCZNIKA

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Streszczenie

Skrobię ziemniaczaną mieszano w podwyższonej temperaturze z roztworem wodnym zawierającym kwas siarkowy, siarczan magnezowy i mocznik, po czym mieszaninę reakcyjną suszono i prażono w temp. 125°C (398 K). W poszczególnych doświadczeniach zmieniano kolejno czas prażenia oraz dawki kwasu siarkowego, mocznika i siarczanu magnezowego. W dalszych badaniach zastępowano również siarczan magnezowy innymi solami, a kwas siarkowy wymieniano na kwas fosforowy. Uzyskano interesujące wyniki wpływu rodzaju i ilości wprowadzanych chemikaliów na lepkość kleików i redukcijność otrzymanych preparatów modyfikowanej skrobi. Rezultaty doświadczeń pośrednio wskazują na sieciowanie skrobi z udziałem doświadczeń pośrednio wskazują na sieciowanie skrobi z udziałem mocznika nie tylko za pomocą wiązań cząsteczek przy węglu C₁, ale również za pomocą poprzecznych wiązań, np. przy węglach C₆. Te ostatnie wiązania poprzeczne powstają również za pośrednictwem reszt fosforanowych.