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Synthesis and properties of carbamoylethyl starch[*)]

Summary — A new ecological and simple method of acrylamide derivatives of starch (carbamoylethyl starch CrES) obtaining, consisting in starch modification using Michael addition reaction in base environment, was elaborated. The course of starch degradation (with the aim to decrease its molecular weight) was investigated as well as the course of substitution reaction of starch with acrylamide dependently on the amounts (concentrations) of bases used (NaOH and KOH). The effects of temperature, reaction time and amount (part) of acrylamide added on degree of substitution (*DS*) were studied. CrES structure was confirmed using the following methods: MALDI TOF, FT-IR spectroscopy, DSC and X-ray diffractometry. Molecular weight distribution of starch modification, what can be controlled by degradation time, was determined using mass spectrometry. Modified starch was well soluble in water and their aqueous solutions, concentrated up to 40%, were obtained. The effects of solution concentration and degree of substitution on the solution viscosity dependently on the shear rate have been studied. The influence of *DS* value and temperature on the solubility of CrES in water has been established too.

Key words: starch modification and degradation, carbamoylethyl starch.

Evolution in modification of polymers and their rapid growth of production in the recent decades became a developing impulse for the new environmentally friendly group of biodegradable plastics. The problems of environmental pollution are not exceptional for the polymers. The total concentration of the polymers in waste products is only 7 wt. %, but the same concentration calculated by volume is 30% [1]. Moreover, some of the waste products obtained from polymers are very hardly tolerated by natural environment. That is the reason why recently the soluble and degradable materials have become attractive. One of them is starch with their modifications.

Starch is not only an important ingredient of human existence, but is used in many other fields. Starch is the most widespread carbohydrate in nature, and occurs in majority of the plants: corn, wheat, white potato (all continents), milo, rice (Asia, America, Europe), tapioca (Asia, South America), arrowroot or sago (Asia). The starch containing plants differ from country to country, depending on the climate and agriculture conditions. Detailed descriptions of the production of commercial starches were published [2, 3]. Plant organisms are known as starch producers [4]. Starch is synthesized and stored by plants in the form of small particles, the starch granules. Starch is actually one of the most actively investigated biopolymers [5]. The structure of starch, consisting of amylose and amylopectin units has already been well characterized [6—9].

Chemical modification (grafting, dextrinization, hydrolysis, esterification, etherification, and oxidation or cross-linking, as well as combined hydrolysis or oxidation and grafting) of starch has become a necessity due to growing demand for novel materials with better properties [10]. Such modifications are efficient enough for the increasing use of starch to provide thickening, binding, gelling, film forming, limiting the emission of toxic formaldehyde, hydro transport in limited drag flow and also to purify proteins in two-phase systems [11—17]. Between all of these modifications, vinyl addition onto starch appears to be a very promising field for research giving good possibilities of improving the properties of starch.

Such ecological modifications can find the application in agriculture and packaging industry because of their easy degradation after certain time of use. Degradation in this context means the lowering of the molecular weight and this process cause that the polymer fragments can be assimilated by microorganisms.

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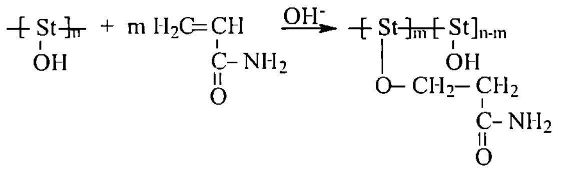
Carbamoylethyl starch (CrES) is one of the most interesting starch modifications. Up to now a lot of methods of carbamoylethyl starch synthesis in the reaction of acrylamide (Aam) with starch (Scheme 1) were published in the literature. One approach was done with the use of organic solvents like cyclohexane, isopropyl alcohol, and dimethylformamide together with water, with the excess of NaOH [18, 19]. Insolubility or low solubility in cold water and low degree of substitution was the problem. That seriously limits the possibility of further applications.



Scheme 1. Alkylation of starch with acrylamide via Michael-type addition

Our proposal presented in this paper is environmentally friendly synthesis — the reaction of starch with acrylamide only in water with smaller amounts of NaOH. Such procedure gives modified starch with almost the same amount of nitrogen and soluble in cold water and degradable.

EXPERIMENTAL

Materials

Potato native starch (PN-A-74710) was obtained from Zakłady Przemysłu Ziemniaczanego (Potato Industrial Works), Piła, Poland. Acrylamide was purchased from Fluka, Switzerland. Sodium hydroxide, potassium hydroxide, methanol, hydrogen chlorine were purchased from P.P.H Polskie Odczynniki Chemiczne (Polish Chemical Reactants), Gliwice, Poland. All the chemicals were used without further purification.

Synthesis

All samples of CrES were synthesized by alkylation of starch with Aam *via* Michael-type addition as follows: 20 g of starch was mixed with 180 mL of distilled water. The slurry was heated to 85°C in a 250-mL three-necked flask provided with thermometer, dropping funnel, condenser and a mechanical stirrer. The starch granules swell and burst and the solution become quite viscous. Various amounts of sodium hydroxide or potassium hydroxide dissolved in distilled water were added to the reaction mixture slowly with intensive mixing. The temperature of the reaction mixture was increased to 90°C and was kept 4 h with stirring. Then the temperature of reaction mixture was lowered and the reaction was carried out in the range 30—80°C. A 50% solution of Aam in water [4g of Aam in 4 mL of distilled water for sample CrES1 (20:4); 7 g of Aam in 7 mL of distilled water for sample CrES2 (20:7); 10 g of Aam in 10 mL of distilled water for sample CrES3 (20:10); 15 g of Aam in 15 mL of distilled water for sample CrES4 (20:15)] was added to the reaction mixture and mixed for 1 to 5 h at various temperatures. The reaction mixture was neutralized by addition of 1M HCl and then precipitated by addition of 200 mL of reaction mixture to 2000 mL of methanol. Methanol proved to be more efficient non-solvent for precipitation of CrES than ethanol or acetone. Finally, the product was dried at 85—90°C, giving 17—19 g of CrES. All organic solvents were constantly recycled by distillation and reused.

Characterization

MALDI TOF

Mass Spectrometer KOMPACT MALDI 4 produced by Cratos Analytical was used for the determination of molecular weight. As a matrix 2,5-dihydroxybenzic acid (DHB) 0.2M water solutions with addition of 0.1 wt. % of CF_3COOH was used. The sample was diluted in 25 mg/mL of distilled water. Before measurements the sample solution was mixed with the matrix in the ratio 1:80 and then poured out (about 1—1,5 μL) on the measuring plate. As a reference insulin (M = 5733 Da) was used and as matrix signal — sinapinic acid (M = 207 Da) with two point calibration.

Elemental analysis

The elemental analysis of all the samples was done using automatic flame analyzer Perkin-Elmer, series II CHNS/O. The estimation of three elements, *i.e.* nitrogen, carbon, hydrogen, has been done.

Fourier Transformation-Infra Red spectroscopy (FT-IR)

The FT-IR spectra of polymers were recorded in solid state using KBr dispersion method in the absorbance mode. All the polymers as well as KBr were properly dried in a vacuum oven and were stored in a desiccator. The FT-IR spectra were recorded with a BIORAD FT-IR 165 spectrophotometer in the range of 4000—400 cm^{-1}. Measurements were carried out at the temperature 25°C. The FT-IR spectra were analyzed with the Bio-Rad Win-IR software.

Differential scanning calorimetry (DSC)

The DSC experiments were done using a Perkin-Elmer DSC 7 with temperature regulator (Perkin-Elmer TAC 7/7) and the cooling system. The average mass of all the samples was about 10 mg. The samples were placed in the aluminum pan, stabilized in temperature 20°C and then heated up with 10°C/min rate until

350°C. As a reference the empty aluminum pan was used.

X-ray diffraction

X-ray diffractograms of all the polymers, acrylamide and starch in powder form were recorded with a DRON 2.0 X-ray diffractometer using FeKα radiation. The conditions were: interstices 1 × 1 × 0.5 mm, 25 kV/15 mA, integrator 400, the scattering angle (2θ) was varied in the range 10—60°.

Rheological experiments

The rheological experiments were conducted by using Mettler RM 180 rheometer at the temperature 25°C for the different shear rates. The measurements were carried out in the coaxial cylinders.

RESULTS AND DISCUSSION

Synthesis

Undegradable modified of starch involve introduction of substituted groups through reactions with the free alcoholic hydroxyl groups of the anhydroglucose units. One is primary on C-6, and two are secondary, on C-2 and C-3. The number of substituted groups introduced is estimated by analysis, and may be expressed as percentage of functional groups as degree of substitution (*DS*). The extent of the reaction in the case of acrylamide is expressed as percentage of nitrogen (%N). Degree of substitution is also given as an alternative way of expressing the extent of reaction. The *DS* was calculated from the nitrogen content of the starch sample as follows [20]:

$$DS = \frac{162 \cdot \%N}{1400 - (71 \cdot \%N)} \qquad (1)$$

Starch modifications with a high *DS* of hydrophobic substituents are water insoluble, but may swell or disperse in certain organic solvents. None of the starch ethers of high *DS* have gained the commercial significance. The major goal of the experimental works was the *DS* increase in the synthesized modifications in basic conditions.

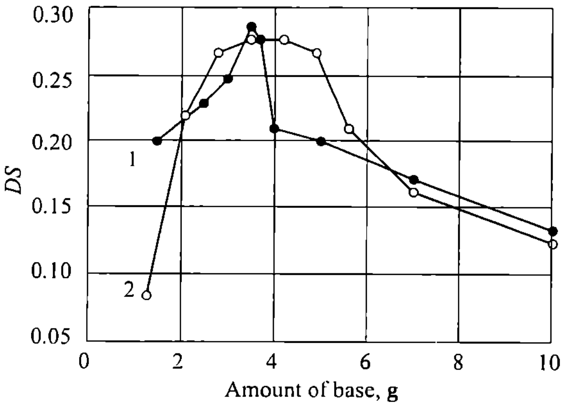


Fig. 1. Effect of NaOH (curve 1) and KOH (curve 2) amounts on carbamoylethylation of starch (starch 20 g, acrylamide 10 g, reaction temperature 50°C, reaction time 2 h)

Figure 1 shows the effect of the amount of NaOH and KOH on the extent of carbamoylethylation of starch. The extent of the involved addition reaction is expressed as degree of substitution. It can be seen that the extent of the reaction at first increases significantly with increasing of NaOH and KOH concentration, reaching its maximum at 3.5 g for NaOH and 3.5-4.2 g for KOH, then decreases. Over these amounts hydrolysis of amide groups (-CONH$_2$) to carboxylic ones (-COOH) takes place with elimination of NH$_3$. The higher degree of substitution can be reached by using NaOH as reaction catalyst. It was confirmed by determination of nitrogen content (Table 1) and degree of substitution in our samples. Both catalysts similarly catalyzed the addition reaction. However, the use of NaOH causes faster hydrolysis of the amide groups in carbamoylethyl starch and acrylamide, than the use of KOH. The carbamoylethyl starch obtained with amount of NaOH equal about 3.5 g shows higher nitrogen content than that obtained with using the higher concentration of NaOH, indicating higher rate of hydrolysis at higher NaOH concentration.

Table 1. Nitrogen content of carbamoylethyl starch obtained in the reaction catylyzed with various amounts NaOH or KOH. Results of elemental analysis*)

NaOH, g	Nitrogen, %	KOH, g	Nitrogen, %
1.5	1.64	1.3	0.64
2.5	1.80	2.1	1.70
3.0	1.96	2.8	2.12
3.5	2.25	3.5	2.17
3.7	2.14	4.2	2.14
4.0	1.89	4.9	2.10
5.0	1.59	5.6	1.65
7.0	1.35	7.0	1.29
10	1.10	10	0.98

*) Starch 20g; acrylamide 10g; reaction temperature 50°C; reaction time 2 h.

Table 2. Nitrogen content of the carbamoylethyl starch obtained at various reaction temperatures and durations*)

Reaction time, h	Temperature, °C					
	30	40	50	60	70	80
	N, %	N, %	N, %	N, %	N, %	N, %
1	0.98	1.12	1.75	1.50	0.98	0.90
2	1.63	2.16	2.25	2.07	1.22	1.01
3	1.67	2.15	2.26	2.04	1.16	0.96
4	1.62	2.11	2.25	2.00	1.12	0.91
5	1.56	1.93	2.07	1.88	0.97	0.72

*) NaOH — 3.5 g

Table 2 shows the variation of nitrogen content of CrES with variation of reaction time at various temperatures. For all samples the nitrogen content increases with increasing the reaction time up to 2 h. Then from 2 to 4 hours remains almost constant indicating that the some of the amide groups of the CrES are slowly converting to carboxyl groups *via* hydrolysis reactions. After 4 h reaction time, the nitrogen content faster decreases indicating higher rate of hydrolysis with increasing reaction temperatures. At 70°C and 80°C the nitrogen content is lower than at 30—60°C, because hydrolysis of the amide groups in Aam and CrES occurs faster at high temperatures. At 30°C the nitrogen content is lower than at 40—60°C, because catalytic process is slow in low temperatures. The high yield of the reaction takes place when the catalytic concentration of NaOH is used for all the CrES polymers.

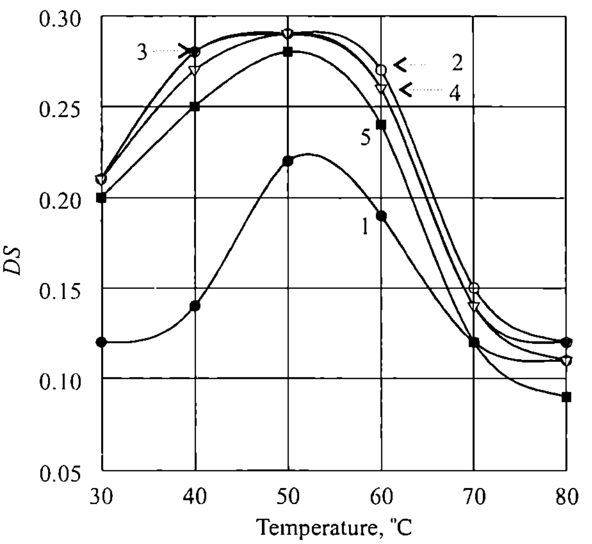


Fig. 2. Dependence of degree of substitution (DS) on the temperature of carbamoylethylation reaction; reaction time (h): 1 (curve 1), 2 (curve 2), 3 (curve 3), 4 (curve 4), 5 (curve 5) (starch 20 g, acrylamide 10 g, NaOH 3.5 g)

Figure 2 shows the effect of the temperature on *DS* of CrES for various reaction durations. For all reaction durations the degree of substitution increases with increase of temperature and reaches maximum value for 50°C. Above this temperature *DS* decreases. Degree of substitution is the lowest for 1 h reaction time for all temperatures. With extension of reaction time the ability to react with acrylamide increases reaching the highest values for 2—4 hours, then decreases. Temperature growth above 50°C and reaction time over 4 hours augments ability to hydrolysis of amide groups in CrES.

As can be seen in Figure 1, the highest *DS* in reaction of modification for CrES was reached for catalytic amount equal to 3,5 g of NaOH. For the all concentration of Aam the effect on the *DS* is proportional. For the higher concentration (*e.g.* 15 g) the increase is still observed but not so spectacular (Table 3). It can result from the fact that for the lower amount of doped Aam the catalytic process dominates. This proved that higher amount of Aam is favorable for the modification process.

T a b l e 3. Effect of the acrylamide amounts on degree of substitution (*DS*) for CrES samples[*]

Aam, g	Nitrogen, %	Carbon, %	Hydrogen, %	*DS*
4	1.01	41.11	6.32	0.12
7	1.74	41.35	6.28	0.22
10	2.47	41.30	6.23	0.33
15	3.21	42.99	6.25	0.44

[*] NaOH 3.5 g; reaction temperature 50°C; reaction time 2 h.

Molecular weight

The molecular weight of the native potato starch, insoluble in cold water, is about $3 \cdot 10^4$ till even $1 \cdot 10^{30}$. The degradation process is demanded for obtaining the soluble products after the modification process with Aam. The degradation time should exceed one hour. The degradation process is carried out until the molecular weight reaches a few thousand units. For the reaction time between one and four hours the controlled degradation can be obtained. This allows the process to be finished at the proper moment and this way one receives the products of quite well defined molecular weight. As a consequence good mass profile can be reached. It can be connected with the sophisticated applications of the polymer (*e.g.* gels and highly viscous aqueous solutions). It is extremely difficult to determinate the exact molecular weight of the starch (and others polysaccharides and their modifications) by the MALDI TOF mass spectroscopy, and because of this fact the profile of the molecular weight is presented.

Figure 3 presents the dispersion of molecular weight for the sample CrES3 in the range 800-3000. Maximum of dispersion occurs in the area of molecular weight for the 1629.6 value (this means ten mers of starch). Near to that signal of characteristic peak for the value 1701.0 is observed originated from substituted Aam. Such whole spectra prove that the etherification reaction of the starch with Aam has been carried out.

This statement is confirmed by rheological experiments. The viscosity of starch solution decreases with the lowering of molecular weight. Degradation process carried out longer than four hours results in the presence of glucose leads to an unexpected product of the modification process (*cf.* Table 5).

FT-IR spectra

In the FT-IR spectra of CrES (Fig. 4), for the wave number in the range of 3500—3000 cm^{-1} characteristic

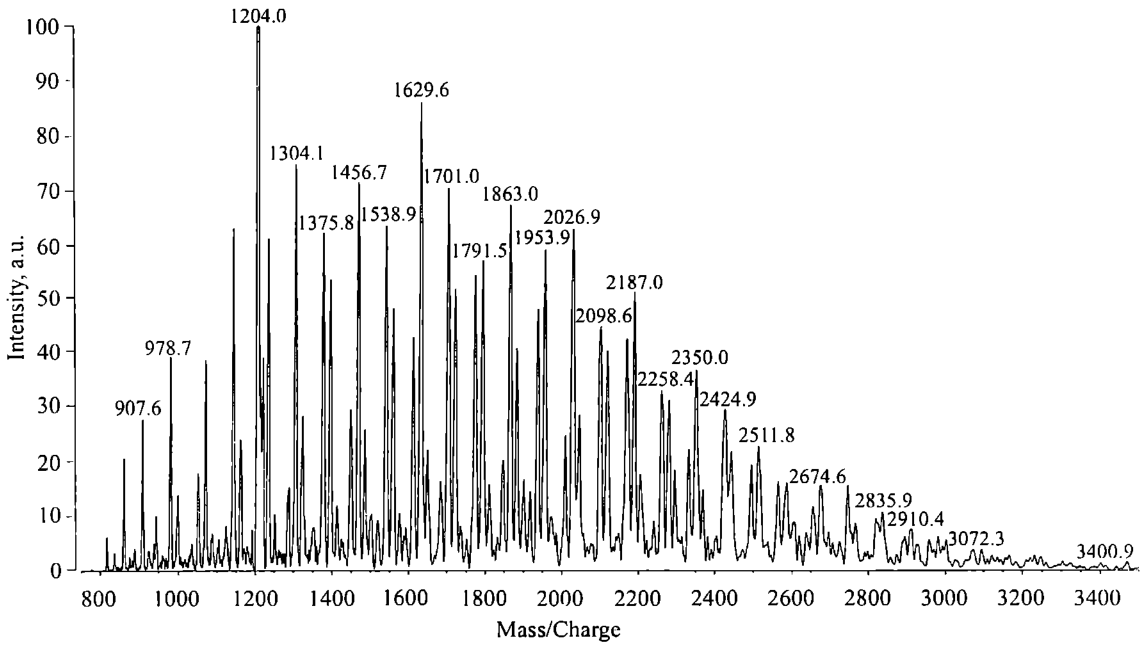


Fig. 3. MALDI TOF spectra of the carbamoylethyl starch (sample CrES3)

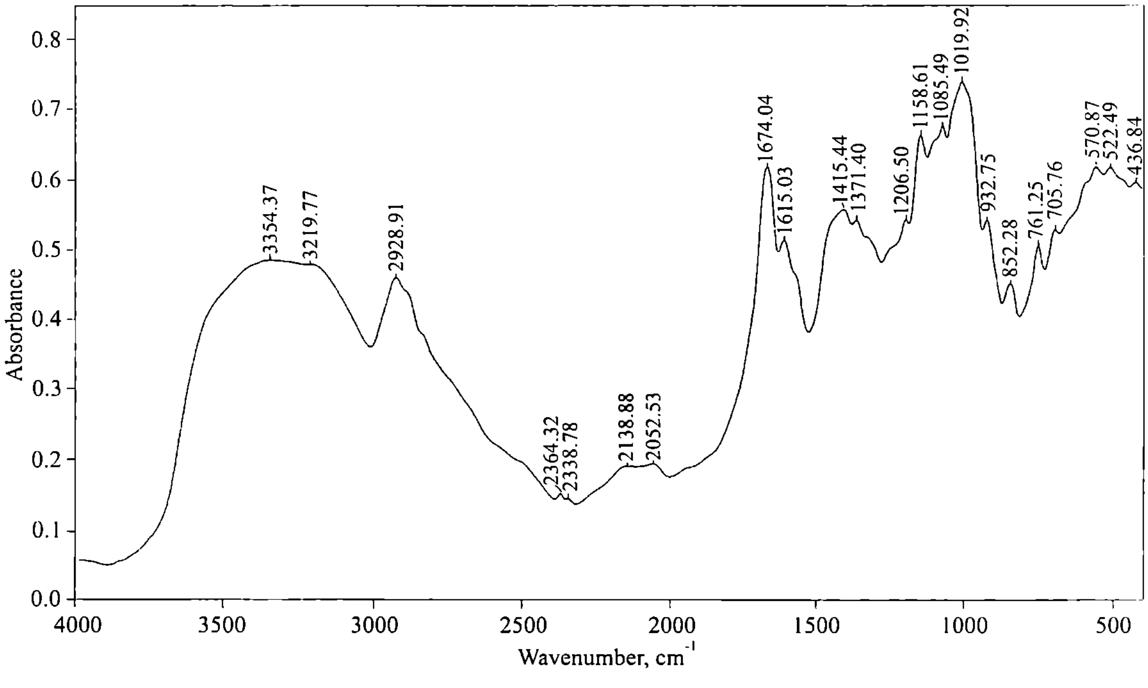


Fig. 4. FT-IR spectra of carbamoylethyl starch

vibration bonds for amides should be observed [free =NH stretching (amide II); bonded =NH stretching (amide II)]. Unfortunately we were not able to analyze them, because of overlapped effect of OH groups originating from starch. Deformation rock vibration of NH group (850 cm^{-1}) is covered by asymmetric C–C vibration originating from starch rings as well. In the range 1420—1330 cm^{-1} characteristic bonds for C–O– stretching, 930 cm^{-1} –OH bending and 2930 cm^{-1} –CH_2 stretching are observed.

The chemical structure of CrES can be determined on the basis of strong signals in the wave number range of 1672—1615 cm^{-1}, originating from I and II amide bonds. In the FT-IR spectra of CrES weak vibration signals occur in the wave number about 1415 cm^{-1}, for –COOH originating from amides hydrolyze. Spectra of ten variously substituted CrES differ from each other by different intensity of the bonds what is especially visible for I and II amide bonds; this is connected with different concentration of amide groups in examined CrES.

Thermal analysis

T_g of CrES is influenced by the groups introduced: carbamoylethyl ones (increasing T_g value) and carboxyl ones, created as a result of $CONH_2$ groups hydrolysis (decreasing T_g value).

The DSC experiments (Table 4) confirm the hypothesis that for the lowest amount of Aam added (sample CrES1) the catalytic process of modification dominates.

Table 4. Values of glass transition temperature (T_g) for CrES samples

Sample	T_g,°C
CrES1	122.5
CrES2	135.3
CrES3	130.4
CrES4	130.1

This is the sample of the lowest degree of substitution (*DS* = 0.12) so of the lowest T_g.

In case of the samples CrES3 and CrES4, showing the highest *DS*, we observe the decreasing of T_g values in comparison with CrES2 sample. The last one shows the maximal T_g what probably results from the balance between the processes of substitution and hydrolysis of the initial starch.

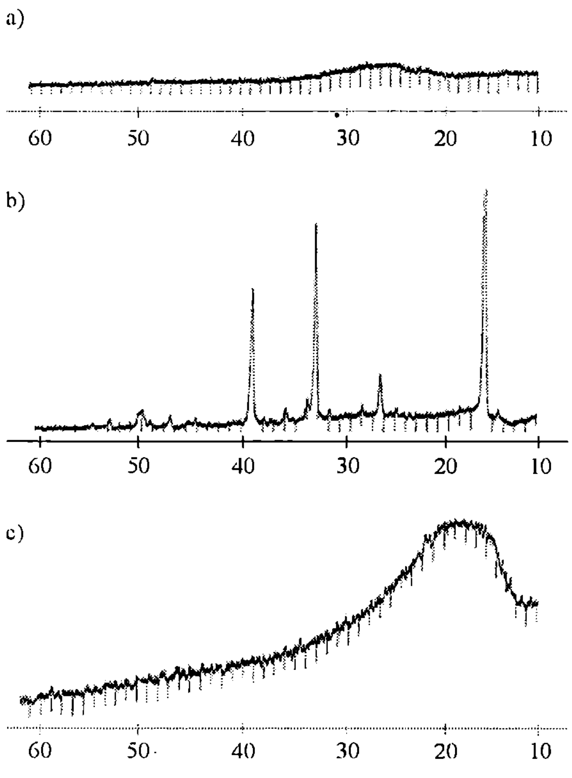


Fig. 5. X-ray diffractograms of (a) starch, (b) acrylamide, (c) carbamoylethyl starch

X-ray diffraction

Starch as a quasi-crystalline material exhibits a number of typical properties characteristic for crystals. Ones of most important are optical properties and among them the ability of forming X-ray spectra and the double diffraction of light. Thanks to mentioned properties it can be assumed that starch has amorphic structure, because of absence of the higher peaks characteristic for crystallinity (Fig. 5a). From the other hand Aam is a typical crystalline substance what is confirmed by the presence of the high and sharp peaks (Fig. 5b). As it can be seen in X-ray spectra the CrES samples are typical amorphous substances and they do not contain the crystalline Aam (Fig. 5c). The crystallinity of the system is not dependent on the degree of addition. As it can be seen from Figure 5 the X-ray experiments confirmed that etherification of starch *via* addition with acrylamide has been done.

PROPERTIES OF CARBAMOYLETHYL STARCH

Viscosity

Table 5. The changes of the viscosity of the solutions during degradation and modification processes as function of time for the initial native starch and the CrES3 sample*)

Time, min	Viscosity, Pa · s	
	Solution, 10%	Solution, 20%
Swell and gelation of initial native starch		
20	0.352	2.800
40	0.721	4.410
60	0.988	5.370
Degradation of initial native starch		
80	0.578	4.660
100	0.231	3.800
120	0.072	2.500
140	0.044	2.050
160	0.034	1.890
180	0.028	1.630
200	0.027	1.350
220	0.025	1.080
240	0.024	0.928
Degradation and modification		
260	0.023	0.755
280	0.022	0.673
300	0.021	0.652
320	0.020	0.650
340	0.019	0.648
360	0.019	0.647

*) Temperature 25°C, shear rate 100 s^{-1}.

Table 5 shows the changes of initial native starch and carbamoylethyl starch (sample CrES3) solution viscosity as a result of swell, gelation, degradation and modification processes. 10 and 20% starch solution were taken for easier analysis of results of rheological experiments. In the early phase (up to 60 minutes) the swelling, gelation and dissolution processes take place as a result of destruction of the hydrogen bonds so the viscosity increases. After that between about 60 and 240 minutes the degradation process of initial starch is carried out and the viscosity decreases. Degradation process is connected with the decrease of molecular weight of starch. Then ability to solubilize of starch increases. After 240 minutes starch was modified for 120 minutes by Aam. A long time of degradation of starch causes that after modification the solubility of obtained CrES in cold water is possible. Even 40% aqueous solution of CrES has been obtained.

The viscosity of aqeous solutions of CrES samples as a function of concentration is shown in Fig. 6. Sample with higher extent of modification (curves 3 and 4) shows higher viscosity value than those with lower extent of modification (curves 1 and 2) for concentrations above 20%. Below this concentration, all the modifications show low viscosity, similar for all samples.

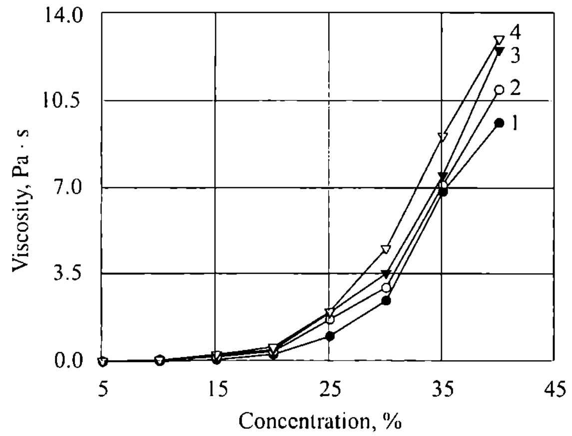


Fig. 6. Effect of the carbamoylethyl starch concentration on the viscosity of its aqueous solutions; samples of carbamoylethyl starch: CrES1 (curve 1); CrES2 (curve 2); CrES3 (curve 3); CrES4 (curve 4); (temperature 25°C, shear rate 100 s^{-1})

The conclusion is that the degree of substitution in high dilution influenced only slightly on viscosity of solutions of modifications. Polymer chains have here more freedom to move in solution. At higher concentration however this freedom of movement sharply decreases, resulting in big differences in viscosities of CrES samples. Final viscosity of modified starch is much lower than in the case of native starch after glue formation, what is shown on Table 5.

These results confirm the fact that starch undergoes chemical and physical changes during its reaction with acrylamide. It was also confirmed in other publication [18]. It is due to lower molecular weight of modification in comparison with native starch. Under the influence of NaOH starch undergoes degradation and its molecular weight reduces. Molecules of CrES, trending to the saturation of remaining free hydroxyl groups, absorb water as a result of solvation, so modified starch undergoes the hydration. As a consequence of hydration, hydrogen bonds between polysaccharide chains are cut off causing micelles fragmentation, what improves their water solubility. Unmodified starch is water insoluble. Native starch creates slurry in water so viscosity measurements are now impossible (first twenty minutes in the Table 5).

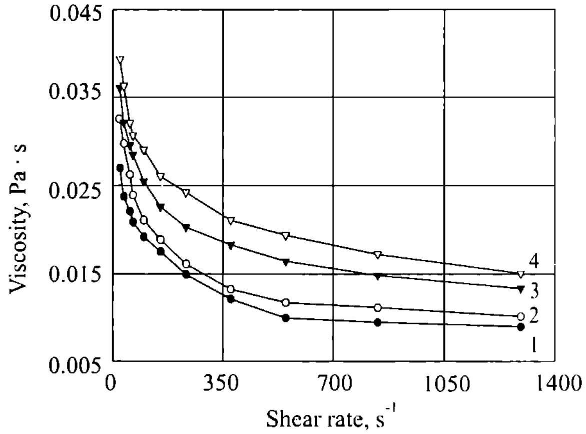


Fig. 7. Effect of the shear rate on the viscosity of aqueous solutions of carbamoylethyl starch; samples of carbamoylethyl starch: CrES1 (curve 1); CrES2 (curve 2); CrES3 (curve 3); CrES4 (curve 4) (temperature 25°C, concentration 10%)

Figure 7 illustrates that when shear rate increases, viscosity of modified starch decreases. The difference between viscosities of CrES1 and CrES4 is evident when shear rates are low. With increasing of shear rate this difference twice decreases. Viscosities of all samples change proportionally independently on the shear rates. Modified starch chains with more carbamoylethyl groups have limited freedom of movement in solution. They form viscous aqueous solutions. It is caused by bigger amount of inter-molecular hydrogen bonds. Low substituted starch chains (CrES1) have unlimited freedom of movement in solution and are able to displace. Even at slight shear rates their viscosities are evidently lower than viscosities of the sample CrES4. Now it is evident that degree of substitution effects viscosity — the higher values of *DS* correspond with the higher viscosity.

Solubility

Solubility in water of carbamoylethyl starch samples prepared under different conditions has been measured at temperatures: 20, 40, 60°C for 60 minutes. The dependence of solubility on the degree of substitution is shown in Figure 8. So, the solubility increases with in-

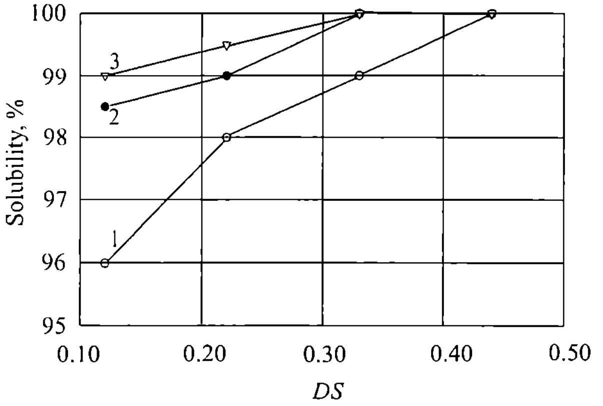


Fig. 8. Solubility (%) of carbamoylethyl starch in water (10 g sample/90 g H2O) at different temperatures versus degree of substitution (DS); temperatures (°C): 20 (curve 1); 40 (curve 2); 60 (curve 3)

creasing of the degree of substitution of the modified starch and at elevated temperatures. The most important from this point of view is degree of substitution ≥0.3. All investigated modifications are well soluble in water due to low molecular weights resulted by starch degradation. As a consequence of this fact, the modified starch solubilities are increasing together with prolongation of the initial time of starch degradation (see Table 5).

CONCLUSIONS

Potato starch is thermodegradable, and observing this process as a function of time we are able to regulate its parameters until the polymer with promising properties for chosen applications is obtained. The processes of gelling and dissolving of modified starch in water can be controlled this way.

Starch reacts easily with acrylamide *via* Michael-type addition reaction under mild conditions. FT-IR spectroscopy, X-ray diffraction and elemental analysis confirmed the structure of CrES obtained.

The excess of basic catalyst (NaOH and KOH) over catalytic amount causes hydrolysis of amide group (–$CONH_2$) to carboxylic one (–COOH) with elimination of NH_3. Hydrolysis process is confirmed by elemental analysis and thermal analysis (DSC). The highest yield of polymer was obtained for amount of NaOH equal 3.5 g, two hours reaction time and reaction temperature 50°C. According to our results, weight ratio NaOH/starch was ten times decreased, amount of acrylamide was twice decreased, but obtained results of nitrogen content are similar to those obtained with the use of organic solvents and for corn starch described in the literature [17—19]. Rheological experiments confirm our results. This is coupled with a generation of amide groups what is confirmed by *DS* values. As a result of hydrolysis the viscosity of the CrES solution decreases what is connected with a decrease of the amount of amide groups in modifications. The obtained modifications after drying and dissolving in cold water create about 40% solutions. The obtained non-toxic, biodegradable modifications with high degrees of substitution are well soluble in water, making industrial environmentally friendly applications possible.

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