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Solid-state thermal reactions of starch with semicarbazide hydrochloride. Cationic starches of a new generation

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Abstract

Starch and semicarbazide hydrochloride heated either convectionally or in the field of microwaves reacted into *O*-(C-carbamoylated) starch. The products retained their hydrochloride salt character making them cationic. Both heating methods provided approximately the same products. The macrostructure of starch reacted on convectional heating was more damaged but degree of reaction on the microwave heating was higher as proven by differential scanning calorimetry, thermogravimetry, scanning electron microscopy, and IR spectroscopy. Reaction products were substantially less sensitive to alpha amylolysis than the original starch was.

Keywords: Starch chemical modification; Starch *O*-(C-carbamoylation); Microwave heating

1. Introduction

Carbamoylation of starch and products of those reactions has evoked a considerable interest, as adhesives, pigmented coatings, surfactants, and their block copolymers are biodegradable. Products obtained in reaction of starch with urea were considered as nitrogen enriched fodder for ruminants. There are several methods of starch carbamoylation (Tomasik & Schilling, 2004). In our recent paper (Siemion, JabŁońska, Kapuśniak, & KozioŁ, 2004), carbamoylation of starch in a solid-state reaction involving convectional and microwave heating was presented. Such modification of starch was then extended to reactions with biuret (Siemion et al., 2004), thiourea (Siemion, Kapuśniak, & KozioŁ, 2005), and guanidine (Siemion & KozioŁ, 2004). In this paper, further extension of the studies of the thermal reactions of starch with derivatives of carbonic acid is presented. A reaction of starch with semicarbazide hydrochloride is described. Reaction of starch with that reagent can provide carbamoylated starch if the protonated hydrazide moiety is a leaving group. On the other hand, if water would be abstracted after attack of the hydroxyl group from the D-glucose unit of starch, novel starch derivatives could be formed. Such a reaction could be called *O*-(C-carbamoylation) of starch. Such a product could retain the basic hydrazido group, and the product could open a route to a new generation of cationic starches, as well as biodegradable materials. Semicarbazones of dialdehydo starch coordinated selectively certain metal atoms into corresponding Werner-type complexes (Para & Karolczyk-Kostuch, 2002), and they could seasonally protect natural pesticides e.g. entomopathogenic nematodes from toxic action of heavy metals (Para & Ropek, 2000). Products of the reaction studied in this paper could compete with semicarbazones of dialdehydo starch.

2. Materials and methods

2.1. Materials

Potato starch (11.2% moisture) was isolated in Potato Enterprise in Niechlów, Poland, in 2003. Semicarbazide hydrochloride of >99% purity was purchased from Fluka Chemie (Buchs, Switzerland). alpha-Amylase from porcine pancreas (EC.3.2.1.1) was purchased from Merck (Darmstadt, Germany).

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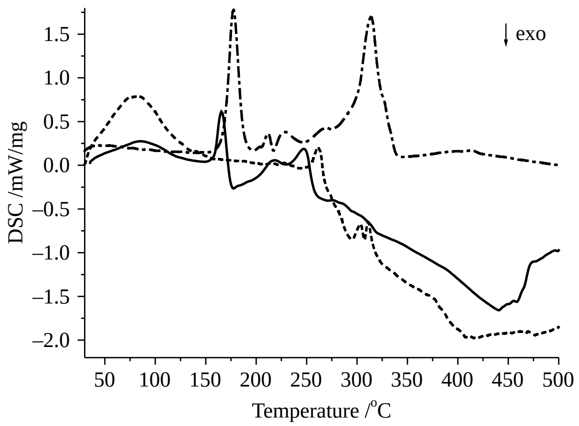


Fig. 1. Differential scanning calorimetry of starch (pointed line), semicarbazide hydrochloride (broken line) and physical mixture of both (solid line).

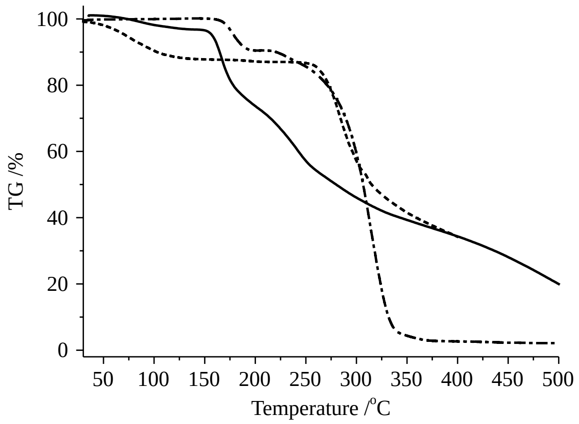


Fig. 2. Thermogravimetric analysis of starch (pointed line), semicarbazide hydrochloride (broken line) and physical blend of both (solid line).

2.2. Methods

2.2.1. Reactions of starch with semicarbazide hydrochloride

Both reagents were blended in 1:1 (mol/mol of D-glucose unit) proportion and either heated in the air for 5 min in a Whirlpool MT221 oven set at 900 W or at 205 °C in an ELF 11/6 Eurotherm Carbolite furnace (Hope, England) for 1 h. These parameters were selected after checking the thermal behaviour of reagents and their 1:1 blend ion heating in the range of 25–500 °C in the STA 409C NETZSCH DSC-TG Simultaneous Thermal Analyser (Selb, Germany). The rate of heating in the air was 5 °C/min.

2.2.2. Elemental analysis for nitrogen

It was performed with a PERKIN–ELMER analyser (Shelton, WA, USA), which provided the ±0.3% precision of the estimation.

2.2.3. FTIR spectra

The spectra were recorded in KBr discs in the range of 4000–400 cm^{-1} using Nexus Nicolete spectrophotometer (Madison, WI., USA)

2.2.4. Scanning electron microscopy (SEM)

SEM micrographs were taken using JEOL 5400 apparatus (Peabody, MA, USA) operating with a secondary electron beam with acceleration gradient of 20 eV.

2.2.5. Aqueous solubility

Solubility tests were carried out according to Richter (Richter, Augustat, & Schierbaum, 1968). The tests were duplicated.

2.2.6. Alpha-amylolysis

Amylolysis was carried out according to Bernfeld (1955). It was run in triplicates.

2.3. Results and discussion

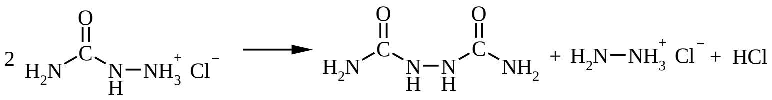
Thermal decomposition of semicarbazide hydrochloride is presented in Fig. 1. The first endothermic effect 177.4 °C was associated with the melting. It was followed by two exothermic effects and the process was completed with irregular endothermic peak which could be considered as a result of the overlap of three effects. Melting of that hydrochloride was accompanied by decomposition as seen in Fig. 2 demonstrating the course the weight loss on heating.

Semicarbazide hydrochloride decomposed into hydrazodikarbonamide and hydrazine hydrochloride as shown below (Nurakhmetov, Beremzhanov, Tashenov, & Erkasov, 1985, 1987) (Reaction 1):

This process assumed the 16.4% weight loss associated with the evolution of hydrochloride. However, experimental weight loss was by more than half lower, reaching hardly 9%.

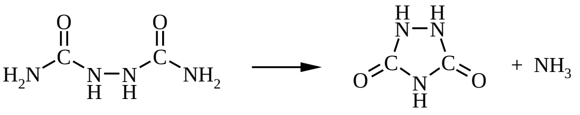
This difference could suggest influence of another process, for instance, recognized (Nurakhmetov et al., 1985; Shtrempler, Murzubraimov, & Rysmendeev, 1982) transformation of hydrazodikarbonamide into urazole (1,2,4-triazolidine-3,5-dione) with evolution of ammonia which could trap hydrochloride (Reaction 2):

The DSC-gram of the physical mixture of starch and semicarbazide hydrochloride (Fig. 1) showed that immediately after melting of the latter at 165.9 °C, an exothermic reaction at 176.7 °C proceeded, and the course of the thermal decomposition of resulting product did not resemble that of plain starch considered in terms of the DSC (Fig. 1) and thermogravimetric (TG) (Fig. 2) analysis. Also peaks characteristic for the thermal



$$2\ \mathrm{H_2N{-}C(=O){-}NH{-}NH_3^+\,Cl^-} \longrightarrow \mathrm{H_2N{-}C(=O){-}NH{-}NH{-}C(=O){-}NH_2} + \mathrm{H_2N{-}NH_3^+\,Cl^-} + \mathrm{HCl}$$

Reaction 1. (Siemion, Kapuśniak, & Kozioł).



Reaction 2. (Siemion, Kapuśniak, & Kozioł).

Table 1
Elemental analysis for physical blend of starch with semicarbazide hydrochloride and reaction products

Sample	Content [%]			
	N	C	H	Cl
Starch, semicarbazide hydrochloride 1:1 mol/mol physical blend	16.22	27.12	5.98	14.20
Product of convectional heating	20.37	43.49	4.40	11.38
Product of microwave heating	21.70	41.04	4.76	12.66

decomposition of semicarbazide hydrochloride did not appear above 250 °C.

Reactions of starch with semicarbazide hydrochloride resulted in considerable increase in the content of carbon and nitrogen, and at the same time in decrease in the content of hydrogen and chlorine (Table 1).

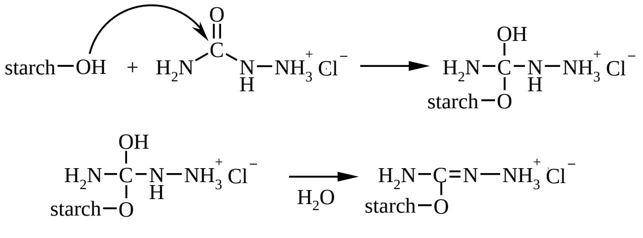
Such changes in the composition implied reaction with evolution of water, possible partial loss of hydrochloride. Based on the course of thermal reaction of starch with urea and biuret, one could assume that in the first stage there was an addition of the starch hydroxyl group to the C=O double bond of semicarbazide as shown below (Reaction 3):

In the obvious reaction, intermediary product stabilized itself with evolution of water. The results of elemental analysis (Fig. 1) fitted such course of the reaction.

Reaction products were free of hydrazine hydrochloride and ammonium chloride and, simultaneously, they were acidic (Table 2). It supported proposed reaction path and the structure of the final product.

Also FTIR spectra (Fig. 3) nicely confirmed assumed reaction course and the structure of the products.

In the FTIR spectra of products, intensive bands over 3000 cm^{-1} could be assigned to the OH and NH_2 stretching vibrations (in the FTIR spectrum of original semicarbazide hydrochloride these bands resided at 3432 and 3255 cm^{-1}). The lower wavenumber side of that broad band decreased, slowly implying an overlap with a commonly broad band assigned to the NH_3^+ stretching vibrations. There was no band, which could be assigned to the amide carbonyl stretching vibrations, which could be anticipated between 1650 and 1700 cm^{-1} (in the spectrum of original semicarbazide hydrochloride intensive band at 1684 cm^{-1} was observed). Instead, there was an intensive band at 1689 cm^{-1} which could be assigned to the C=N stretching modes. The spectra for the products prepared on convectional and microwave heating were very similar, and only in few details they resembled the spectrum of the original starch. The most essential differences of both reaction products were encountered in the region between 990 and 1200 cm^{-1}. In this region, there was the band most characteristic for starch complex, assigned to the bending OH groups, hydrogen bonds and starch phosphate. This band almost completely ceased after reaction heated convectionally, and it could be observed in the microwave-heated product. It suggested that convectional heating was more critical for the macrostructure of starch than microwave heating. Nevertheless, chemical structure of both products resembled one another.



Reaction 3. (Siemion, Kapuśniak, & Kozioł).

Table 2
Solubility in water, pH and conductivity of 1% aqueous solutions of *O*-(C-carbamoylated) starches

Sample	pH	Conductivity (μS/cm)	Solubility (%) (°C)		
			25	50	75
Original starch	7.03	13		2.0	
Convectionally heated starch[a]	7.12	30	1.4	7.4	72.4
Microwave heated starch[a]	6.22	123	89.0	92.0	93.4
Semicarbazide hydrochloride	2.53	9980			
Product from convectional heating	2.95	3790	9.4	9.7	13.1
Product from microwave heating	2.96	4860	8.4	9.8	12.1

[a] Potato starch processed identically but without semicarbazide hydrochloride.

Scanning electron micrographs (Fig. 4) confirmed that convectional heating damaged starch granules to a higher extent than the microwave heating. In both cases, granular structure of starch after reaction was significantly reduced. At 25 °C, the reaction products were by almost 500% more

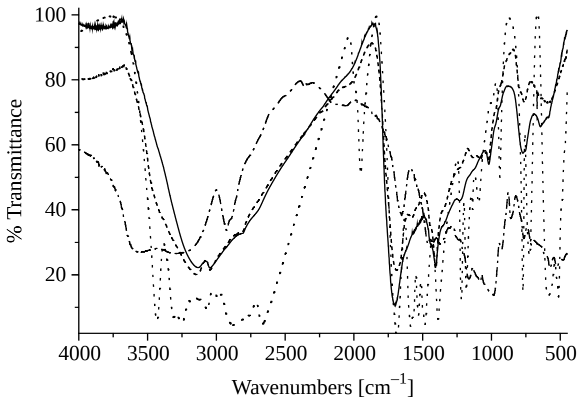


Fig. 3. FTIR spectra of starch (dash dot line), semicarbazide hydrochloride (dot line), product from convectional heating (solid line), and product of microwave heating (pointed line).

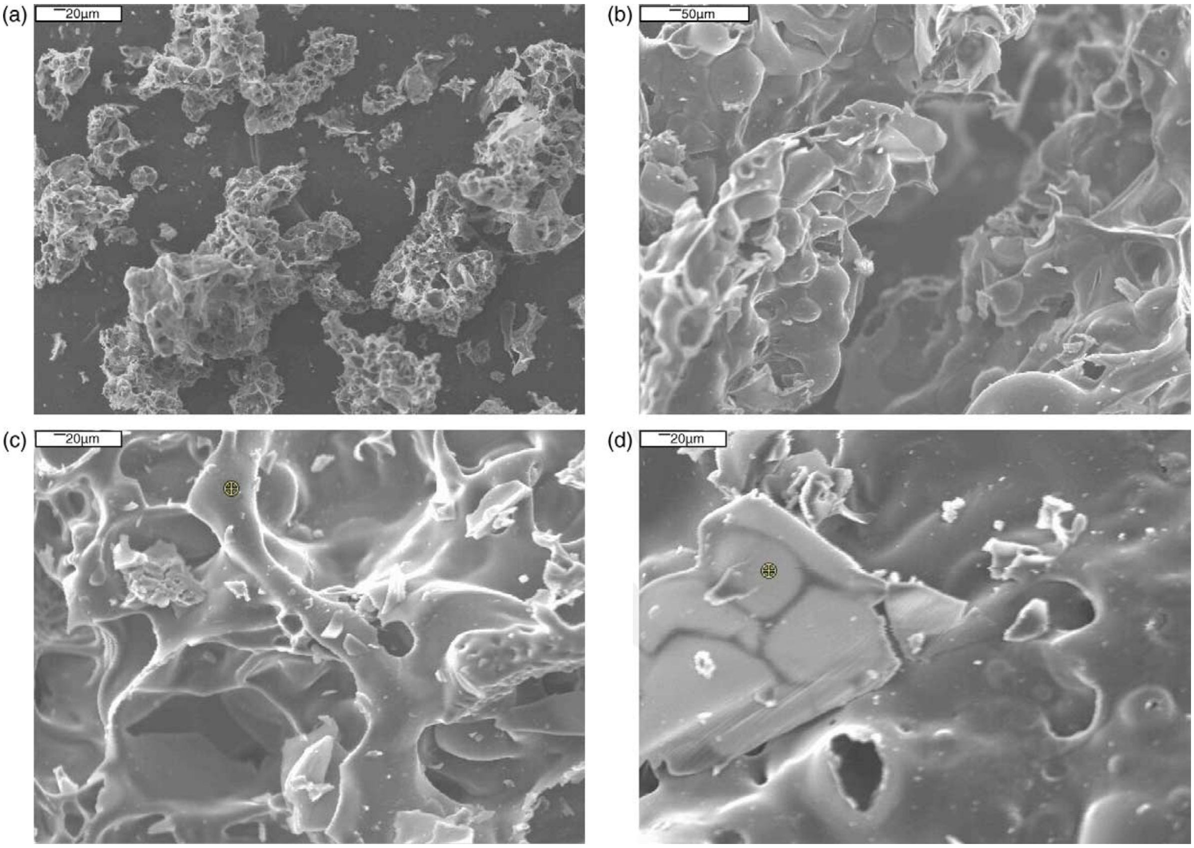


Fig. 4. Scanning electron micrographs of the products from convectional (a and c) and microwave (b and d) heating (a and b, magnification 100×; c and d, magnification 1000×).

water-soluble than original starch as well starch heated for 1 h at 205 °C. Limited solubility of carbamoylated starch from microwave heating, in comparison to solubility of starch heated without amide, could be interpreted as a result of crosslinking of starch. Results of this study negated crosslinking as a dominating process but it might not be rejected as a side-reaction. Solubility of both *O*-(C-carbamoylated) products only slightly increased with temperature to reach hardly around 13% at 75 °C (Table 2).

Conductivity of solutions increased with the content of the cationic substituent in the product but the solubility of the products reflected the extent of the damage of the macrostructure (Table 2).

Fig. 5 presenting comparative thermal decomposition of both reaction products shows that indeed the product prepared by convectional heating decomposed faster and to a higher extent than the second product. These differences might result not only from the degree of destruction of

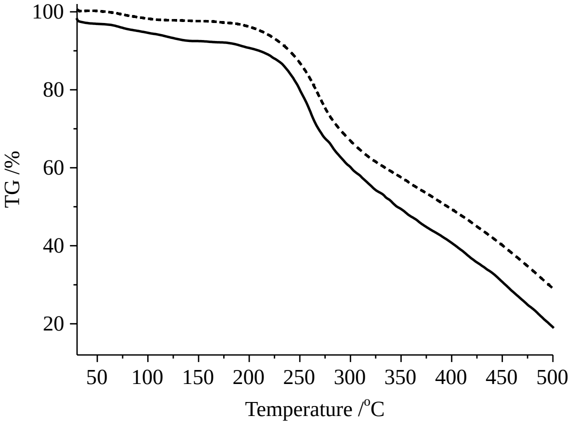


Fig. 5. Thermogravimetry of the products from the convectional (solid line) and microwave (pointed line) heating.

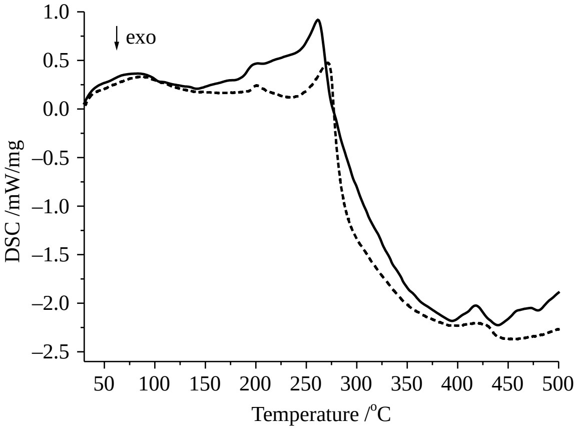


Fig. 6. Differential scanning calorimetry of the products from convectional (solid line) and microwave (pointed line) heating.

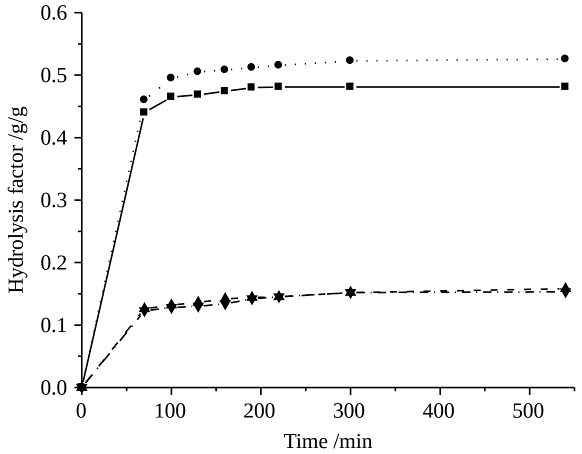


Fig. 7. Course of alpha-amylolysis of unprocessed starch (rhombs), starch heated without reagent (squares), product from convectional (up directed triangles) and microwave (down directed triangles) heating.

the macrostructure but also from the degree of conversion of starch.

Elemental analysis of the products (Table 1) and DSC-grams (Fig. 6) pointed to the latter being higher in case of the product prepared in the microwave-mediated reaction. On the DSC-gram of the product from convectional heating, there was a weak exothermic peak at 143.2 °C suggesting that the reaction of starch with semicarbazide was not completed.

Susceptibility of both *O*-(C-carbamoylated) products to alpha-amylolysis was substantially lower than that of starch and starch heated under the same conditions but without reagents. In terms of hydrolysis factor, both products had practically the same susceptibility reaching hardly 30% of that estimated for plain starch (Fig. 7). Heating of starch without reagent reduced that susceptibility hardly by 10%.

Decrease in the value of hydrolysis factor could result from the introduction of a high number of the novel functional groups as well as from a low pH (2.95–2.96) (Table 2) of the samples.

3. Conclusions

Granular potato starch and semicarbazide hydrochloride heated either convectionally or in the field of microwaves reacted into *O*-(C-carbamoylated) starch. Both heating methods provided closely the same cationic products. The convectional heating damaged starch granules to a higher extent than the microwave heating as proven by FTIR Spectroscopy and Scanning Electron Microscopy. The elemental and thermal analyses showed that degree of reaction in the field of microwaves was slightly higher than on convectional heating. Both products with retained basic hydrazido group could open a route to a new generation of cationic starches. Moreover the susceptibility to α-amylolysis with simultaneous low solubility in water made these products suitable as biodegradable materials.

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