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Solid state reaction of starch with thiosemicarbazide

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Abstract

Potato starch reacted with thiosemicarbazide when convectional and microwave heated. In the preliminary step, hydrazodithioamide was formed. Subsequently, hydrazodithioamide reacted with starch into *O*-hydrazodithioamidostarch and hydrazinostarch isothiocyanate, as proven by thermogravimetric analysis, differential scanning calorimetry, FTIR spectra taken for the products in the solid KBr solution and evolved gaseous products, elemental analysis, scanning electron microscopy and alpha-amylolysis. The microwave heating offered a deeper conversion of the reaction mixture than did the convectional heating. The reaction products were less susceptible to alpha-amylolysis than original starch.

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Keywords: Hydrazinostarch isothiocyanate; *O*-hydrazodithioamidostarch; Starch thiocarbazoylation

1. Introduction

Carbamoylation of starch (Tomasik & Schilling, 2004; Tomasik, Fiedorowicz, & Para, 2004) provides nitrogen containing starches; these starches have invoked considerable interest as fodder, containing bioacceptable nitrogen, for ruminants, paper sizes, depressants in selective flotation of complex metal ores (Drzymała, Tomasik, Sychowska, & Sikora, 2002; Kapuśniak & Tomasik, 1999), polyurethane foams and thermoplastic urethanes (Spychaj & Wilpiszewska, 2004). The functional groups present in such materials offer further modifications with involvement of oxidation and/or crosslinking. Such materials are proposed to be used in fire-resistant construction boards, and sizes for cellulose fabrics. In the synthesis of such kind of products: isocyanates, acrylamides, acrylonitrile and ureas were used (Tomasik & Schilling, 2004).

The costs involved with the chemical modification of starches, providing such derivatives, usually are too high to allow them to be competitive with other products. However, recently, a series of papers was published in which microwave heating provided a facile route to starch modification. The reactions proceeded in the solid state. Recently, the reactions of starch with: urea and carboxylic esters (Sikora, Tomasik, & Pielichowski, 1997b), amino acids (Kapuśniak, Ciesielski, Kozioł, & Tomasik, 1999; Kapuśniak, Ciesielski, & Tomasik, 2001; Kapuśniak, Siemion, & Tomasik, 2003), hydroxy acids (Kapuśniak, 2004; Sikora, Tomasik, & Pielichowski, 1997a), urea and biuret (Siemion, Jabłońska, Kapuśniak, & Kozioł, 2004), thiourea (Siemion, Kapuśniak, & Kozioł, 2005b), guanidine (Siemion & Kozioł, 2004) and semicarbazide (Siemion, Kapuśniak, & Kozioł, 2005a) were described.

In this report, the solid state, microwave assisted reaction of starch with thiosemicarbazide is presented. Reaction of starch with thiosemicarbazide invoked our interest, among others, because of different behaviour of urea and thiourea in such reactions (Siemion et al., 2004, 2005a).

2. Materials and methods

2.1. Materials

Potato starch (11.2% moisture) was isolated in Potato Enterprise in Niechlów, Poland, in 2003. Thiosemicarbazide

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of >99% purity was purchased from Sigma–Aldrich (Steinheim, Germany). α-Amylase from porcine pancreas (EC.3.2.1.1) was purchased from Merck (Darmstadt, Germany).

2.2. Methods

2.2.1. Reactions of starch with thiosemicarbazide

Both reagents were blended in 1:1 (mole/mole of D-glucose unit) proportion and either heated in the air for 5 min in a Whirlpool MT221 oven set for 900 W or at 185 °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 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. Thermogravimetry coupled with infrared spectroscopy (TG/FTIR)

The measurements were carried out in an Al_2O_3 crucible under argon in the temperature range of 25–620 °C with the rate of the temperature increase of 10 °C/min. A Bruker IFS 66 FTIR instrument (Ettlingen, Germany) was used together with a NETZSCH TG 209 (Selb, Germany) thermal analyser.

2.2.4. Fourier transformation infrared spectra (FTIR)

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

2.2.5. 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.

2.2.6. Aqueous solubility

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

2.2.7. pH

The pH was measured in 1% aqueous suspensions at 25 °C. The measurements were run in triplicate.

2.2.8. Conductivity

The conductivity was measured in 1% aqueous suspensions at 25 °C.

2.2.9. Alpha-amylolysis

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

3. Results and discussion

Thiosemicarbazide **(1)** melts with decomposition between 181 and 183 °C (Handbook of physical chemistry, 1974) and hydrazodithioamide **(2)** is the decomposition product (Nurakhmetov, Beremzhanov, Tashenov, & Erkasov, 1987) apart from liberated molecule of hydrazine. At elevated temperature, hydrazodithioamide **(2)** turns into dithiourazole **(3)** of m.p. 221–223 °C.

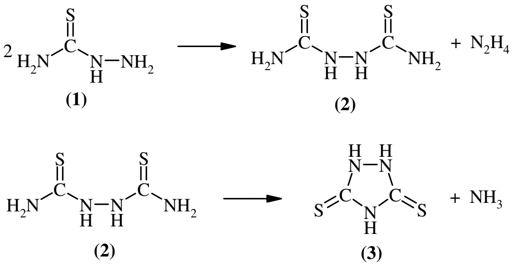


Fig. 1 presenting the analysis of gaseous products of the thermal decomposition of thiosemicarbazide confirmed that course of reaction. There is a clear peak of hydrazine around 3250 cm^{-1}.

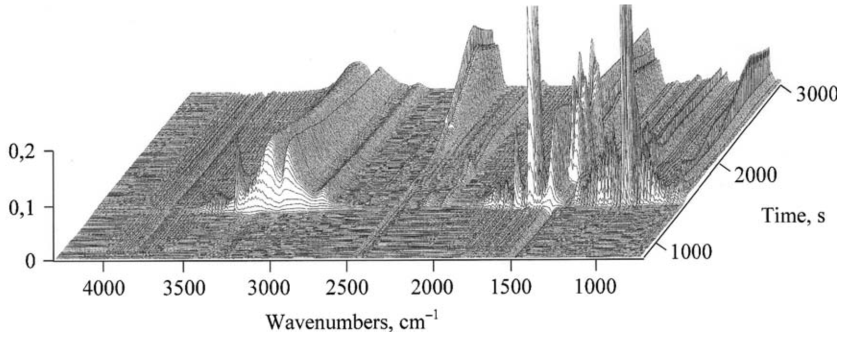


Fig. 1. FTIR analysis of gaseous products of the thermal decomposition of thiosemicarbazide.

Fig. 2 presents the course of the thermal decomposition of **(1)**. The first endothermic effect was immediately followed by the exothermic effect associated with formation of **(2)**. The weight loss began with melting and its total magnitude of 27% corresponded to that calculated for both steps.

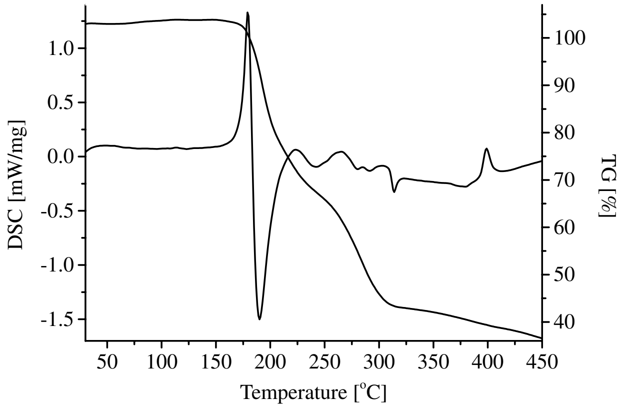


Fig. 2. The thermal behaviour of thiosemicarbazide.

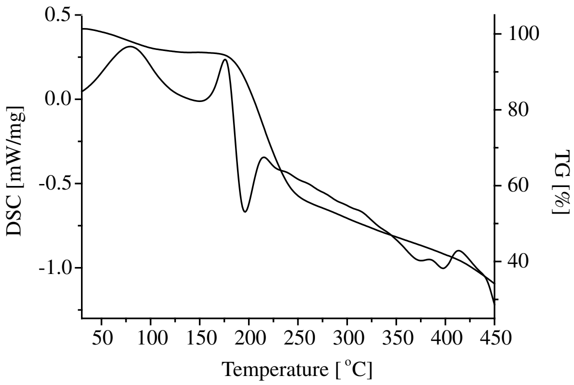


Fig. 3. The course of thermolysis of the equimolar starch – thiosemicarbazide blend.

The thermogravimetric (TG) and differential scanning calorimetric (DSC) monitoring of the behaviour of the equimolar blend of potato starch (calculated for one D-glucose unit) with thiosemicarbazide showed that the first thermal effect appeared at 180 °C (Fig. 3). Thus, it was likely that molten **(1)** as well as **(2)** could react with starch. Quantitative characteristics of that reaction is also given in Table 1.

Heating of starch with **(1)** resulted first in endothermic effect centred at 79.2 °C. That effect was associated with evolution of 11.2% water. The subsequent effect at 176 °C corresponding with melting of **(1)** and, possibly, its transformation into **(2)** overlapped with another effect at 196.1 °C. The latter occurred at a temperature of 6 °C higher than the corresponding effect of formation of **(2)** from pure **(1)**. Therefore, it could be likely, that the observed effect reflected a reaction of **(2)** with starch. Higher-temperature fragments of the diagrams (Fig. 3) did not show any effects which could be related to **(2)** and **(3)** supporting the former assignment of the effect to the reaction of starch with **(2)**. An insight in Table 1 revealed that there were no thermal effects which could be ascribed to decomposition of starch. It additionally confirmed reaction of **(2)** with starch.

Convectional and microwave heating of starch with thiosemicarbazide resulted in different products. Table 1 as well as Figs. 4 and 5 show that the product of the reaction, carried out in the field of microwave, was more thermally stable. The products of convectional and microwave heating began to decompose at 142 and 187 °C, respectively.

In the case of the first product, temperature of the beginning of decomposition was associated with the beginning of a weak endothermic effect, followed by a series of exothermic effects with their minimum at 366.6 °C. The course of the TG line (Fig. 4) allowed two stages of decomposition to be distinguished. The rate of the first stage was clearly

Table 1
Quantitative characteristics of the thermal behaviour of potato starch, thiosemicarbazide and their equimolar blend as well as products of the reaction of starch with thiosemicarbizde carried out on convectional and microwave heating

Sample	TG		DTG	DSC	
	t_i [°C]	Δm [%]	t_p [°C]	t_o [°C]	t_p [°C]
Potato starch (I)	33.3	11.20	71.0	29.9	83.4 (endo)
	246.1	33.79 (46.26)		254.0	261.0 (endo)
			286.2	282.6	294.9 (exo)
	307.3	35.15 (81.29)		303.0	307.5 (exo)
Thiosemicar-bazide (II)	165.2	26.97	191.8	165.9	179.3 (endo)
	211.5	9.47 (35.77)	218.4	183.2	190.2 (exo)
	242.1	24.45 (60.22)		242.1	265.6 (endo)
			283.7	280.4	284.7 (endo)
				308.2	313.9 (exo)
				392.6	398.9 (endo)
Physical mixture of I + II	40.3	6.32	71.4	35.0	79.2 (endo)
	178.7	36.85 (43.19)	214.5	161.8	176.0 (endo)
	248.4	34.54 (77.73)		183.0	196.1 (exo)
Product of convectional heating	142.4	49.04	230.3	205.7	366.6 (exo)
	407.2	25.69 (76.20)	496.2		
Product of microwave heating	187.4	68.73 (69.93)	246.6	232.1	346.7 (exo)

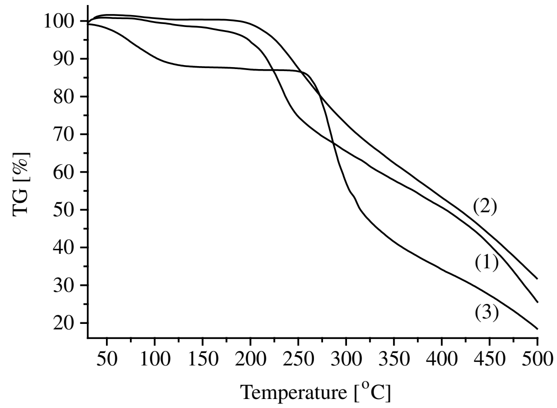


Fig. 4. TG curves for products of reaction of starch with thiosemicarbazide carried out on convectional (1) and microwave (2) heating. Thermal decomposition of original starch is illustrated by curve (3).

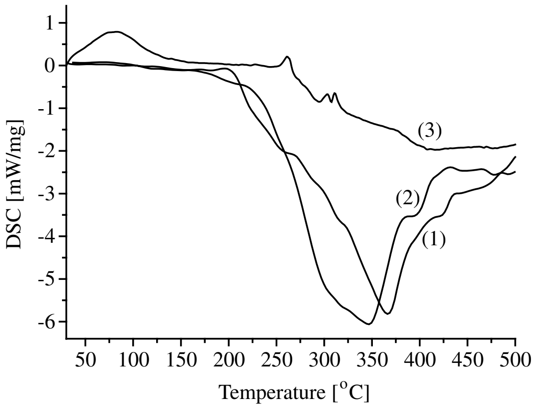


Fig. 5. Differential scanning calorimetry (DSC) of the reaction products from convectional (1) and microwave (2) heating. DSC curve for original starch (3) is added for comparison.

Table 2
Elemental analysis of the reaction products

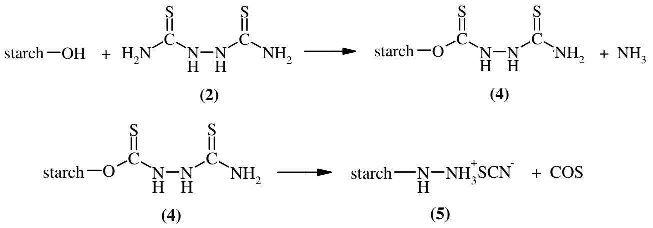
Sample	Content [%]			
	N	C	H	S
From convectional heating	15.82	37.14	5.24	11.35
From microwave heating	13.04	42.88	5.20	8.98
Theoretical values for the starch[a]: thiosemicarbazide 1:1 blend	16.60	33.20	5.93	12.65

[a] Calculated for one D-glucose unit (162 g).

higher. In the case of the second product, after a slow stage of decomposition between 180 and, approximately, 220 °C; next fast decomposition was associated with the beginning of a strong exothermic effect, with its minimum at 346.7 °C.

Table 2 presents the results of the combustion elemental analysis.

Changes in the content of particular elements suggested the following course of reactions. On convectional heating **(2)** was formed, which subsequently was attacked by the hydroxyl group of starch as shown below. The resulting product underwent rearrangement with liberation of COS.



$$\text{starch}-OH + H_2N-\overset{S}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2 \longrightarrow \text{starch}-O-\overset{S}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2 + NH_3$$

(2) **(4)**

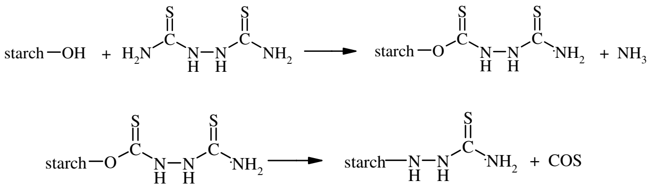
$$\text{starch}-O-\overset{S}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2 \longrightarrow \text{starch}-\underset{H}{N}-N\overset{+}{H_3}SCN^- + COS$$

(4) **(5)**

Liberation of COS was confirmed by the FTIR analysis of volatile products (Fig. 6). The blood-red colour developed in reaction with $FeCl_3$ could point to the formation of the thiocyanate salt (rhodanide) **(5)**. This supports the reaction course presented above, however, thiosemicarbazide also developed red colour with $FeCl_3$.

In that spectrum, peaks characteristic for COS could be noted at 2050 cm^{-1} (Hesse et al., 1984). Evolution of ammonia was also seen around 3000 and 900 cm^{-1}.

In contrast to that, the microwave heating resulted in the reaction following another path, as shown below:



$$\text{starch}-OH + H_2N-\overset{S}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2 \longrightarrow \text{starch}-O-\overset{S}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2 + NH_3$$

$$\text{starch}-O-\overset{S}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2 \longrightarrow \text{starch}-\underset{H}{N}-\underset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2 + COS$$

The course of reactions could be supported by FTIR spectra, which fitted the assumed structures of the products.

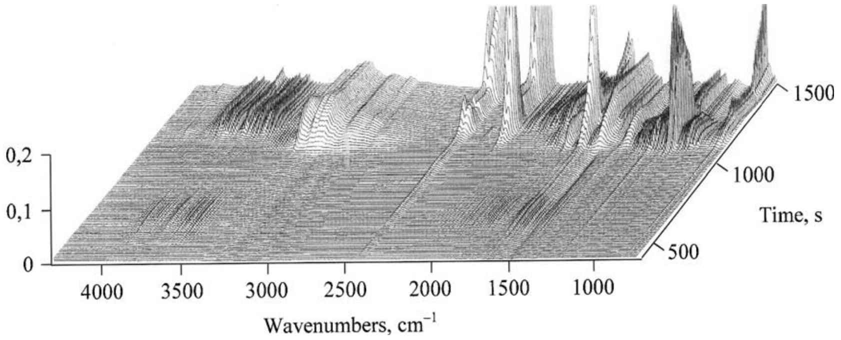


Fig. 6. FTIR analysis of gaseous products liberated on the reaction carried out on convectional heating.

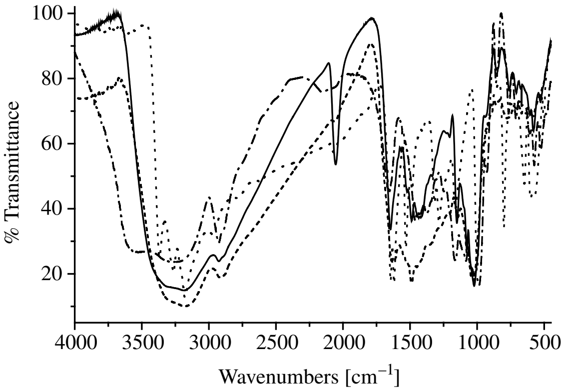


Fig. 7. FTIR spectra of starch (dash dot line), thiosemicarbazide (dot line), product from convectional heating (solid line), and product of microwave heating (pointed line).

In the FTIR spectrum (Fig. 7) of the product, from convectional heating the intensive, high-wavenumber, broad band, could include the band of the NH_3^+ stretching vibrations. The medium intensity peak at 2055 cm^{-1} was characteristic for the SCN^- ion (Hesse et al., 1984) and the N—H stretching vibrations were hidden in the intensive, broad band above 3000 cm^{-1} (the product gave positive test in the rhodanide reaction with $FeCl_3$). In the spectrum of thiosemicarbazide, there was only a very weak band around 2055 cm^{-1}. In the spectrum of the product, from the reaction conveyed on microwave heating, that band was also residual. It indicated that the reaction predominating on convectional heating was only a side reaction on the microwave heating. In the FTIR spectrum of the product, from the microwave heating, the band at 1488 cm^{-1} might not

Table 3
Selected properties of the products of the reaction of starch with thiosemicarbazide

Sample	pH	Conductivity [μS/cm]	Solubility [%]		
			25 °C	50 °C	75 °C
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
Thiosemicarbazide	5.55	271			
Product from convectional heating	5.68	1463	69.52	70.64	76.56
Product from microwave heating	5.29	425	34.64	41.60	50.56

[a] Potato starch processed identically but without thiosemicarbazide.

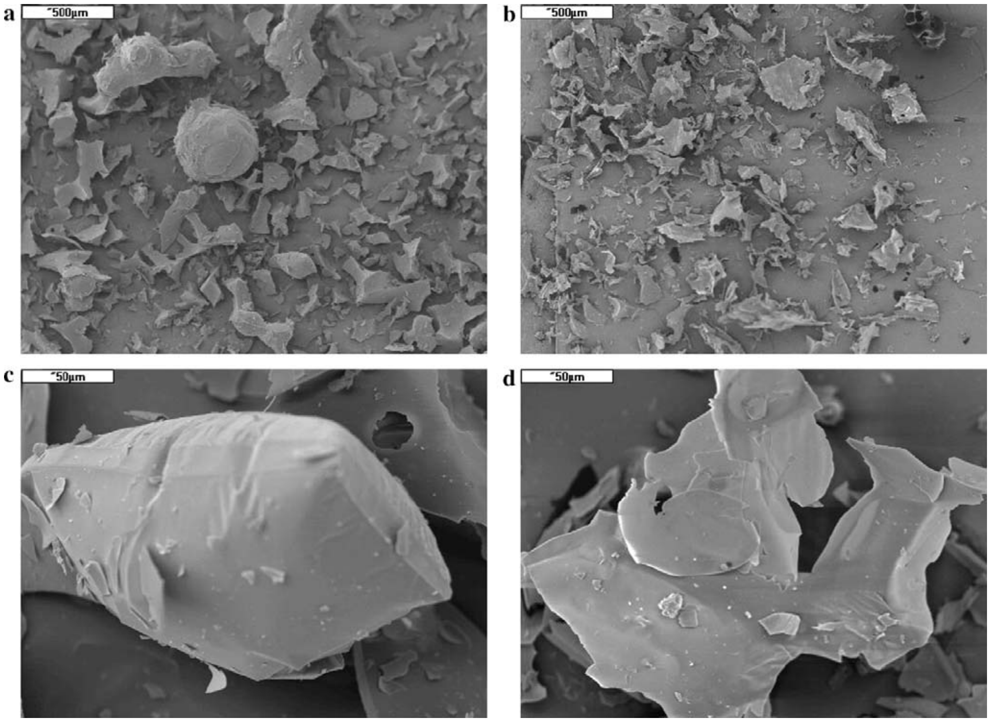


Fig. 8. Scanning electron micrographs of the products from convectional (a, c) and microwave (b, d) heating (a, b – magnification 50×; c, d – magnification 500×).

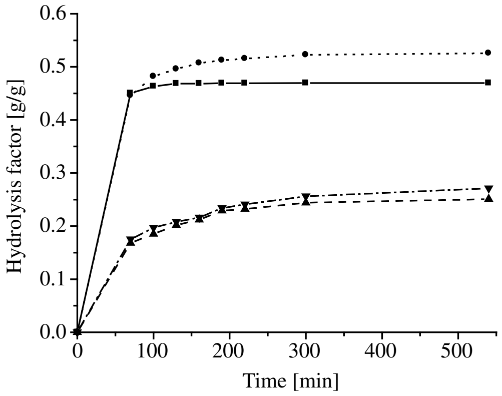


Fig. 9. Course of alpha-amylolysis of unprocessed starch (●), starch heated without reagent (■), product from convectional (▲), and microwave (▼) heating.

be assigned to the —HN—CS—NH— thiocarbonyl group as the same band could be seen also in the spectrum of the product from convectional heating, as well as, in the spectrum of starch. It was likely, that the anticipated vibration of the C=S group was hidden in the group of bands seen in the spectrum of starch. Other characteristic bands belonged to the vibrations in the polysaccharide moiety. It could also be seen that the spectra of both reaction products did not resemble the spectrum of thiosemicarbazide.

Results of the elemental analysis fitted the proposed structures assuming that the degree of substitution was 0.93 and 0.885 for the products from convectional and microwave heating, respectively.

Selected physical properties of both products are collected in Table 3.

An essential difference in solubility and conductivity of aqueous solutions of both products additionally confirmed the assumed salt structure of the product of convectional heating. The conductivity of aqueous solution of (**5**), which was approximately five times higher than that for the aqueous solution of thiosemicarbazide and three times higher in respect to that for the aqueous solution of the reaction product, from the microwave assisted reaction, spoke in favour of structure (**5**). Better aqueous solubility of the latter product also supported its ionic character.

The SEM micrographs (Fig. 8) revealed a deep destruction of the granules. The microwave heating (Fig. 8b and d) was more destructive than the convectional heating (Fig. 8a and c).

The product of the reaction of starch with thiosemicarbazide was essentially less sensitive to alpha-amylolysis (Fig. 9). The heating mode had a minor effect on that.

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