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Microwave-assisted silication of potato starch

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abstract

Silication of potato starch was performed by microwave irradiation and convectional heating of starch with sodium metasilicate. The study has shown that microwaves offered more selective silication than convectional heating. Depending on the dose of metasilicate products of either monoesterification or crosslinking esterification were formed. Increase in the amount of the silicating agent favoured crosslink-ing of starch. In the case of microwave irradiation, the C–O–SiO_2Na moieties were formed, whereas the convectional heating generated the C–O–Si–O–Si–O–C crosslinks.

Keywords: Microwave-assisted reactions, Potato starch, Silication

1. Introduction

Silicon-containing materials and polymers are used all over the world in a variety of industries, domestic products and high technology applications (Ganachaud, Boileau, & Boury, 2008). Among them there are also silicon-based starch derivatives. Generally, they are prepared from starch and either silanes, siloxanes or polysiloxanes (Tomasik & Schilling, 2004, and references therein). Resulting silylated starch derivatives have been checked as adhesives, binders, coatings, water-repellent sizes, among others for paper, glass-fiber sizes and flocculating agents (Billmers, 1990; Lidén, Karlsson, & Tokarz, 2001; Smith, 1985). At the same time, water-soluble silicates, often called inorganic polymers, have been found suitable for synthesis of silicon-based starch derivatives (Blount, 1978; Falcone & Sams, 1978). They are inexpensive, fire and vermin resistant, recyclable materials which, due to the inclusion of condensed macroanions with strong silicon–oxygen bonds, provide excellent strength for the products in which they are used.

Since the last decade of the 20th century, special attention has been paid to layered silicates. Incorporation of the latter, eventually after chemical modification, into the biodegradable starch matrix, i.e., the preparation of nanocomposites, attracted increasing attention in material science research (Sinha Ray & Bousmina, 2005). The biodegradable nanocomposites possess several advantages which make them competitive to other materials for specific uses such as packaging (Avella et al., 2005) or in biomedical applications (Oliviera, Malafaya, & Reis, 2003).

Recently, a number of authors have reported a facile methods of chemical modifications of starch that use microwave irradiation (Biswas et al., 2008; Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005; Lewandowicz et al., 2000; Mao, Wang, Meng, Zhang, & Zheng, 2006; Muzimbaranda & Tomasik, 1994; Xing, Zhang, Ju, & Yang, 2006). Starch esters of inorganic acids are available from the esterification of starch with corresponding acids and their derivatives in microwave-assisted reactions. In such manner starch could be sulphated (Staroszczyk, Fiedorowicz, Zhong, Janas, & Tomasik, 2007; Staroszczyk & Tomasik, 2005), selenated (Staroszczyk, Tomasik, Janas, & Poreda, 2007), and borated (Staroszczyk, 2009). In this study solid state silication of starch with sodium metasilicate performed by microwave irradiation is presented. The study involved recognition of the effects of varying reaction time, microwave power and silicating agent amount on the products composition.

2. Experimental

2.1. Materials

Native potato starch (13% moisture) was isolated in Potato Enterprise in Łomża (Poland). Over 97% sodium metasilicate pentahydrate, was purchased from Fluka.

2.2. Preparation method

Potato starch and metasilicate were blended at 1:0.05, 1:0.1, 1:0.25, 1:0.5 and 1:1 (mole D-glucose unit/mole metasilicate) ratios and thoroughly homogenized in an agate mortar. Final blends (2 g) were irradiated in the Samsung M1711N microwave oven either for 30 min at 450 W or for 5 min at 800 W. For comparison, all

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samples were convectionally heated in the LG MC-8084 NLC oven at 100 °C for 120 min. All reaction products without any purification were stored in tightly closed vessels.

2.3. Thermal analysis (TG, DTG, DTA)

Samples (100 mg) were heated in corundum crucibles in an oven from room temperature up to 1000 °C, at a rate of 10 °C/min. Corundum particles of $\varphi = 8$ μm served as the standard. Paulik–Paulik Erdey D-1500-Q (Budapest, Hungary) instrument was used. Analyses were run in duplicates.

2.4. Fourier transformation infrared spectroscopy (FT-IR)

The FT-IR spectra of samples (3 mg) in KBr (300 mg) discs were recorded in the range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}, using the Matson 3000 FT-IR (Madison, Wisconsin, USA) spectrophotometer.

2.5. Scanning Electron Microscopy (SEM)

Granule morphology of starch samples was run with E-SEM XL30 (FEI Company, Eidhoven, The Netherlands) instrument equipped with a SE detector of secondary electrons. The instrument set for 15 kV accelerating voltage operated at low vacuum. The magnification range changed from 500 to 3000 times.

2.6. Powder X-ray diffractometry

Crystalline structure of the samples was estimated according to Gerard, Colonna, Buleon, and Planchot (2001). The measurements were carried out by applying CuK_α radiation of wavelength 0.154 nm in a Philips type X'pert diffractometer (Eindhoven, The Netherlands). The operation setting for the diffractometer was 30 mA and 40 kV. The spectra over the range of 5.0–60.0° 2θ were recorded at a scan rate of 0.02° 2θ/s.

2.7. Differential scanning calorimetry (DSC)

The samples (~8 mg) were sealed in stainless steel pans with water at the 1:3 weight ratio and left for 1 h for equilibration. They were then scanned at the rate of 6 °C/min in the temperature range of 20–90 °C. An instrument, self-assembled in the Department of Physics of the University of Agriculture in Cracow, Poland, was used with a water filled pan as a reference. Analyses were run in triplicates.

2.8. Aqueous solubility and water binding capacity

Aqueous solubility (AS) and water binding capacity (WBC) at room temperature were estimated according to Richter, Augustat, and Schierbaum (1968). Estimations were run in quadruplicates.

3. Results and discussion

Silication of potato starch was performed either by microwave irradiation or convectional heating of starch with sodium metaslilicate blended at various proportions. In none of the microscopic examinations any objects which could be identified as non-reacted metasilicate were observed. Therefore, the products were analyzed under the assumption that sodium metasilicate completely reacted with starch. This was confirmed by microscopic observations.

3.1. Microscopic observations

Although starch granules deteriorated, regardless of the mode of their heating (Fig. 1) starch silicated with lower doses of metasilicate had distinct, clearly identified, oval-shaped granules. Long exposure of the granules to microwaves of lower power was more destructive to them than short exposure of the granules to high power microwaves. The samples silicated with higher doses of metasilicate did not reveal any granular structure.

3.2. Progress of the reaction

Figs. 2 and 3 present thermograms of native potato starch and sodium metasilicate, respectively. A fast, one-step decomposition of starch took place at 277 °C with the loss of 26.73% of its weight within the range of 161–352 °C (Table 1). On heating up to 174 °C, sodium metasilicate lost gradually two water molecules and was then practically stable up to 970 °C. The 17% weight loss corresponded to that calculated.

Fig. 4 demonstrates TG and DTG curves of the starch silication products prepared by the microwave irradiation for 30 min at 450 W, applying different doses of sodium metasilicate. The TG curves (Fig. 4A) displayed two distinct regions of the weight loss, which were reflected by two peaks on the DTG curves (Fig. 4B), suggesting that the starch silication products revealed at least two-step decomposition. There was a characteristic peak of starch in the range of 161–352 °C – the first step of decomposition, and another peak related to a deep thermolysis of starch, in the region of 352–528 °C – the second step of decomposition. Temperature in their minimum depended on the dose of silicating agent applied. The products prepared by convectional heating also decomposed in two steps, but their TG (Fig. 5A) and DTG (Fig. 5B) curves differed, to a certain extent, from those recorded for the products prepared with the microwave irradiation. When the higher doses of silicating agent were used, a stage of dehydration of the silicate portion of the product could be observed. That stage was fairly rapid in products designed with the assistance of microwaves whereas they were more diffused in the products from convectional heating, showing that microwaves offered more selective silication of starch.

Table 2 shows the course of the thermal decomposition of all products. One could see that convectional heating of starch and its exposure to the microwave irradiation increased temperature of the decomposition in the range of 161–352 °C, while temperature of the first step decomposition of starch silication products decreased gradually with increasing amount of sodium metasilicate applied. Additionally, decomposition temperature of the microwave-synthesized products were lower than these of the convectionally heated products. An increasing amount of sodium metasilicate taken to the reaction implied an increasing water content. As the water content increased, temperature of the first step of decomposition of the products decreased, particularly for those obtained in the microwave field. However, the highest doses of silicating agent, equivalent to over 20% water content in the blend, caused an increase in decomposition temperature. Temperature of the second step of decomposition of starch silication products also decreased with an increase in the dose of sodium metasilicate. Thus, the amount of sodium metasilicate, and its water, affected temperature of the reaction system and that trend followed former findings (Lewandowicz, Fornal, & Walkowski, 1997).

On increase in the dose of the silicate reagent, the slope (tg α) of the TG line in the range of 161–352 °C decreased regardless of the reaction conditions applied, showing that the silication of starch was not very selective. Metasilicate concentration dependent changes of the decomposition rate (tg α) suggested that the starch:metasilicate = 1:1 provided the most homogenous product.

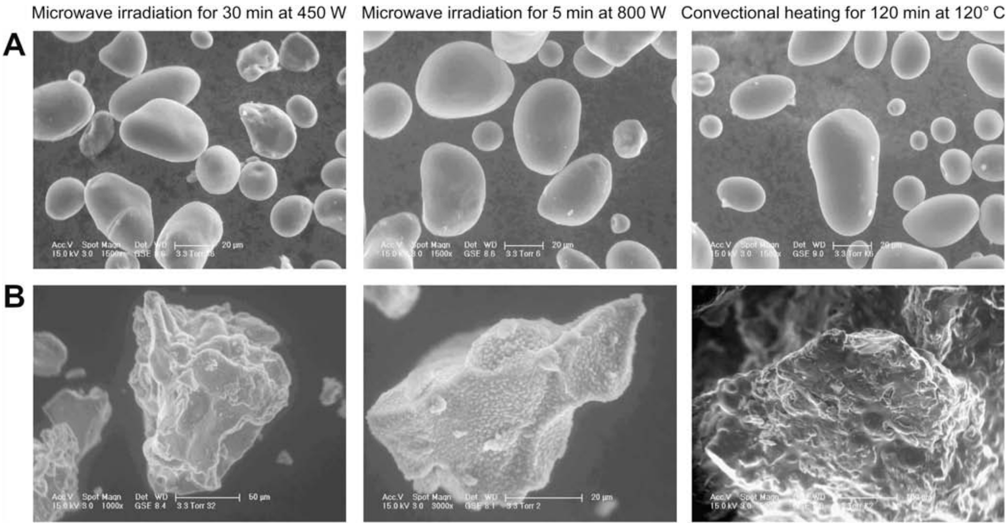

Fig. 1. The scanning electron micrographs of silicated starch samples from silication on microwave irradiation and convectional heating of 1:0.05 (A) and 1:1 (B) blend.

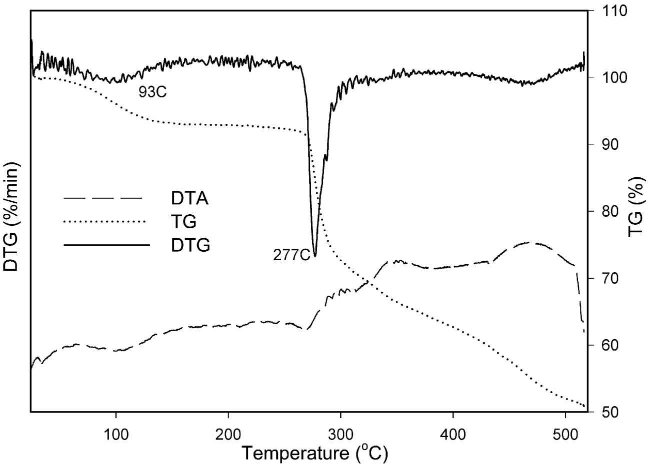

Fig. 2. Thermogram of native potato starch.

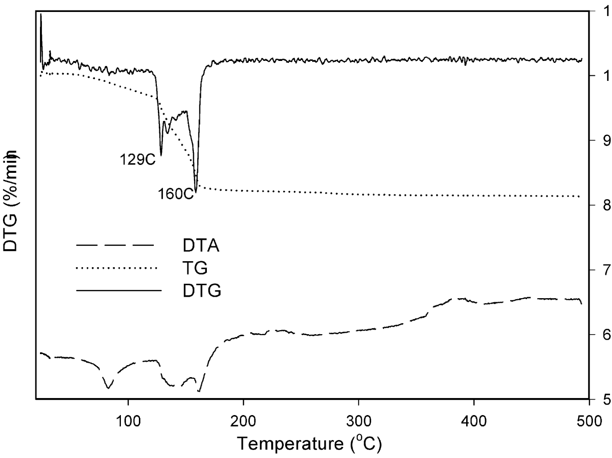

Fig. 3. Thermogram of sodium metasilicate pentahydrate.

The weight loss associated with the second step of decomposition initially declined with an increasing dose of the silicating agent, but it increased again when 1:0.25 starch:sodium metasilicate proportion was applied. The data in Table 3 show that when 1:0.05 and 1:0.1 proportions of the reagents were used, the experimental weight loss in the range of 352–528 °C was lower than that calculated from the thermograms of particular components of the products, and the weight loss found from the thermograms in the range of 25–161 °C was comparable to that calculated. In the cases of 1:0.25, 1:0.5 and 1:1 proportions, the experimental weight loss in the range of 352–528 °C exceeded that calculated, and simultaneously the experimental weight loss in the range of 25–161 °C was significantly lower than that calculated. It could suggest again that the amount of water introduced with hydrated sodium metasilicate affected the reaction system.

FT-IR spectroscopy provided analysis of the behaviour of sodium metasilicate pentahydrate treated by convectional heating and microwave irradiation. Corresponding assignment of the spectral bands of metasilicate prior to and after its microwave irradiation presented in Fig. 6 is given in Tables 4 and 5.

Hydrated alkali silicates consist of a mixture of polymeric and oligomeric silicates and are largely protonated due to the weakness of silicic acid (Garcia, Ingram, & Bazan, 2002). There were marked differences between the relevant spectra. Absorption intensity at 1636 cm^{-1}, attributed to the bending vibrations in HOH, decreased with dehydration taking place on microwave irradiation. Simultaneously, the fundamental vibrations for silica structure strongly changed. The intense band at 985 cm^{-1} which was observed in the spectrum of hydrated metasilicate, in the spectrum of metasilicate irradiated for 30 min at 450 W decreased and split into two bands, at 969 and 1028 cm^{-1}, reflecting the stretching vibrations of the Si–OH (Neves, Lenza, & Vasconcelos, 2002) and asymmetric stretching vibrations of the Si–O–Si bonds (Uchino, Sakka, & Iwasaki, 1991), respectively. The band at 866 cm^{-1} in the spectrum of microwave irradiated metasilicate attributed to an overlap of bending and stretching vibrations of the Si–OH bond (Uchino, Sakka, Hotta, & Iwasaki, 1989) shifted towards higher wave number (894 cm^{-1}), suggesting an involvement of the silanol groups in the hydrogen-bonding. The bands at 1120, 777 and 636 cm^{-1} disappeared, whereas the band at 459 cm^{-1} increased in the intensity and shifted towards lower wave numbers (417 cm^{-1}) as a result of the microwave irradiation of hydrated metasilicate.

Hence, on microwave irradiation of sodium metasilicate pentahydrate, H–Na exchange reaction progressed as follows:

$$\equiv \text{Si—ONa} + H_2O \rightarrow \equiv \text{Si—OH} + OH^- + Na^+ \qquad (1)$$

Table 1
Thermogravimetric characteristics of native potato starch and sodium metasilicate.

Sample	Temperature range (°C)	Weight loss[a] (%)	Slope[b] (tg α)	DTG (°C)
Potato starch	25–161	7.00		96
	161–352	26.73	1.11	277
	352–528	15.69		
	528–970	1.64		
	Total	51.06		
Sodium metasilicate pentahydrate	25–117	2.70		
	117–145	6.99		129
	145–161	5.00		160
	161–174	2.31		
	174–352	1.09		
	352–528	0.60		
	528–970	0.50		
	Total	19.49		

[a] Percentage of weight loss during the specified temperature ranges.
[b] The slope of TG line.

and formed hydroxyl ions reacted with Si–O–Si, causing the breaking of the latter, which can be described by:

$$\equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{OH}^- \rightarrow \equiv \mathrm{Si{-}OH} + \equiv \mathrm{Si{-}O}^- \qquad (2)$$

and SiO$^-$ ions formed from reaction (2) could then react with another water molecule:

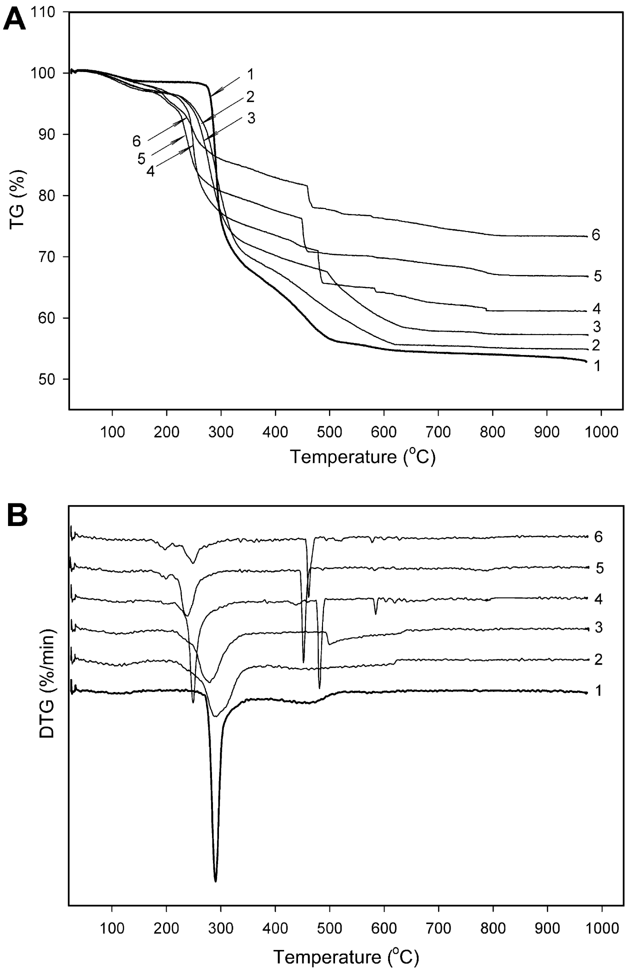

Fig. 4. TG (A) and DTG (B) curves of starch (1) and starch blended with sodium metasilicate at proportions 1:0.05 (2), 1:0.1 (3), 1:0.25 (4), 1:0.5 (5), 1:1 (6) for the microwave irradiation time of 30 min and the power of 450 W.

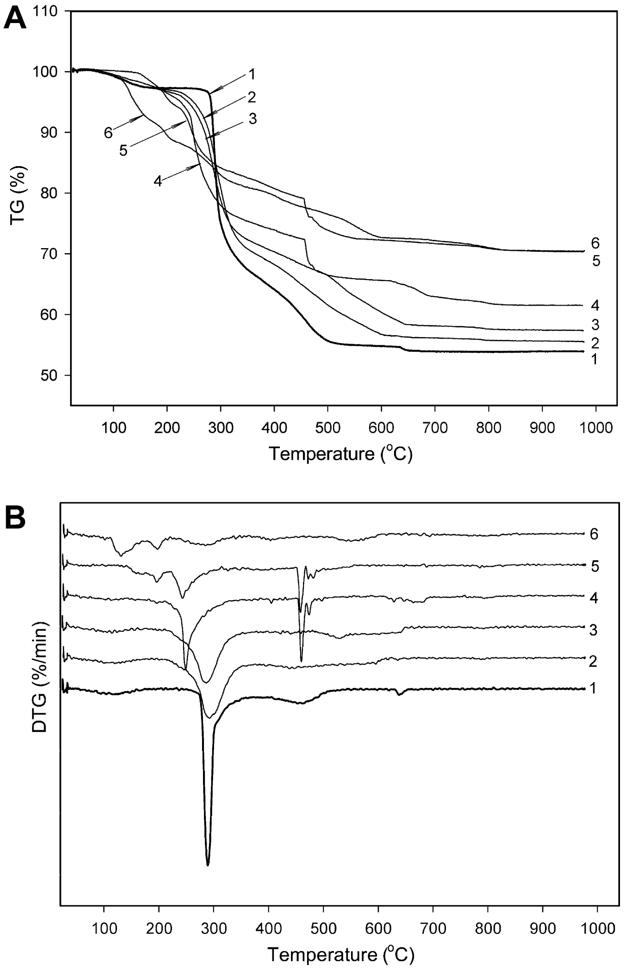

Fig. 5. TG (A) and DTG (B) curves of starch (1) and starch blended with sodium metasilicate at proportions 1:0.05 (2), 1:0.1 (3), 1:0.25 (4), 1:0.5 (5), 1:1 (6) for the convectional heating time of 120 min at 100 °C.

$$\equiv \mathrm{Si{-}O}^- + \mathrm{H_2O} \rightarrow \equiv \mathrm{Si{-}OH} + \mathrm{OH}^- \qquad (3)$$

The FT-IR studies confirmed also the formation of new Si–O–Si bonds, according to reactions (4) and (5).

$$\equiv \mathrm{Si{-}OH} + \mathrm{OH{-}Si} \equiv \rightarrow \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{H_2O} \qquad (4)$$

$$\equiv \mathrm{Si{-}O}^- + \mathrm{HO{-}Si} \equiv \rightarrow \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{OH}^- \qquad (5)$$

The spectra of native potato starch and starch blended with sodium metasilicate at 1:0.5 and 1:1 proportions, and modified in various conditions, are presented in Figs. 7 and 8, respectively. The band assignments for potato starch are given in Table 4, and the spectral characteristics of all starch silication products are presented in Table 5.

The broad O–H stretching vibrations observed between 3700 and 3000 cm^{-1} in the spectrum of starch turned more narrow as the silication progressed, and ultimately, in the spectra of the products prepared at the 1:0.5 proportion, a quite narrow band could be observed, independently of the conditions of the silication (Fig. 7). Simultaneously, there were essential changes in the shape and relative intensity of the bands in the range of 2000–400 cm^{-1}. The strong absorption band at around 980 cm^{-1}, observed in the spectrum of either heated or irradiated starch, shifted towards higher wave numbers and split into two maxima, at around 995 and 1019 cm^{-1} in the spectra of silicated starch samples. On one hand it has already been reported that the peak at 995 cm^{-1} was sensitive to the moisture content

Table 2
Thermogravimetric characteristics of starch silication products.

Sample	Temperature range (°C)	Microwave irradiation						Convectional heating		
		30 min at 450 W			5 min at 800 W			120 min at 100 °C		
		WL[a] (%)	Slope[b] (tg α)	DTG	WL (%)	Slope (tg α)	DTG	WL (%)	Slope (tg α)	DTG
Potato starch										
	25–161	1.35			2.99			2.55		
	161–352	30.7	1.40	291	28.81	1.36	298	30.13	1.71	290
	352–528	11.98			13.84			12.21		
	528–970	2.98			1.11			1.19		
	Total	47.01			46.75			46.08		
Potato starch:sodium metasilicate										
1:0.05	25–161	2.98		113	3.34		112	2.58		112
	161–352	27.02	0.43	291	25.92	0.42	290	26.71	0.43	294
	352–528	10.25			10.33			10.75		
	528–970	4.84			3.68			4.4		
	Total	45.09			43.27			44.44		
1:0.1	25–161	2.69		109	3.47		108	2.52		113
	161–352	25.34	0.42	279	24.82	0.49	260	25.23	0.41	287
	352–528	7.53		499	8.45		500	7.77		530
	528–970	7.08			5.15			7.1		
	Total	42.64			41.89			42.62		
1:0.25	25–161	1.95			2.72		112	2.04		
	161–352	23.12	0.83	249	22.12	0.59	242	22.63	0.65	250
	352–528	9.65		481	9.15		476	9.18		460, 473sh
	528–970	4.18		585	4.94		577	4.62		
	Total	38.90			38.93			38.47		
1:0.5	25–161	2.75		199	3.24		198	1.07		196
	161–352	18.15	0.36	239	17.46	0.39	235	16.47	0.25	243
	352–528	8.87		452	8.6		450	9.42		458, 478sh
	528–970	3.45			2.83			2.48		
	Total	33.22			32.13			29.44		
1:1	25–161	1.97		197	2.24		195	7.49		131, 198
	161–352	13.59	0.21	248	12.74	0.18	254	5.59		
	352–528	7.45		461	7.7		466	5.18		
	528–970	3.68			4.21			5.33		
	Total	26.69			26.89			23.59		

[a] Percentage of weight loss during the specified temperature ranges.
[b] The slope of TG line.

Table 3
Found and calculated weight losses associated with the second step of decomposition (in the range of 352–528 °C) of starch silication products.

Sample[a]	Temperature range (°C)	Weight loss (%)					
		Microwave irradiation				Convectional heating	
		30 min at 450 W		5 min at 800 W		120 min at 100 °C	
		Found[b]	Calculated[c]	Found	Calculated	Found	Calculated
1:0.05	25–161	3.0	2.2	3.3	3.7	2.6	3.3
	352–528	10.3	11.3	10.3	13.0	10.2	11.5
1:0.1	25–161	2.7	2.8	3.5	4.3	2.5	3.9
	352–528	7.5	10.7	8.5	12.3	7.8	10.9
1:0.25	25–161	2.0	4.6	2.7	5.9	2.0	5.5
	352–528	9.7	9.2	9.2	10.6	9.2	9.4
1:0.5	25–161	2.8	6.6	3.2	7.6	1.1	7.4
	352–528	8.9	7.5	8.6	8.6	9.4	7.6
1:1	25–161	2.0	8.9	2.2	9.6	7.5	9.4
	352–528	7.5	5.5	7.7	6.3	5.2	5.6

[a] Potato starch:sodium metasilicate.
[b] Found from the thermogram.
[c] Calculated from experiments with individual components.

(Van Soest, de Wit, Tournois, & Vliegenthart, 1994), and the peak at 1022 cm^{-1} has been assigned to the amorphous region of starch (Liu, Charlet, Yelle, & Arul, 2002; Sevenou, Hill, Farhat, & Mitchell, 2002). On the other hand, this split band belonging to starch overlapped with the band belonging to hydrated sodium metasilicate observed at 985 cm^{-1}, also shifted to 1028 and 989 cm^{-1} after irradiation at 450 and 800 W, respectively. Thus, the shift towards higher wave numbers of both these bands, corresponding to the bending vibration of the COH moiety in starch and the stretching vibration of Si–O in sodium

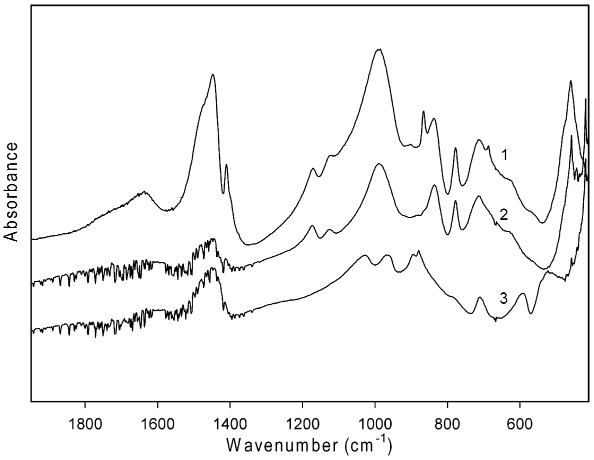

Fig. 6. FT-IR spectra of sodium metasilicate pentahydrate: unmodified (1), microwave irradiated at 800 W for 5 min (2), and microwave irradiated at 450 W for 30 min (3).

metasilicate, could suggest their interaction and the formation of the C–O–Si bonds in silicated starch samples.

After treatment of starch with the highest dose of sodium metasilicate by both convectional heating and microwave irradiation, the products showed a much broadened band in the region between 3700 and 3000 cm^{-1}, and a broad absorption band at about 880 cm^{-1} adjacent to the band at around 1000 cm^{-1} (Fig. 8). This clearly confirmed that a large proportion of water was incorporated into silicated starch, as determined by the thermal analyses, and new hydrogen bonds were formed with hydroxyls, silanols and water molecules. Furthermore, while the microwave-synthesized silicated starch revealed at least three characteristic bands in the region between 1000 and 1200 cm^{-1}, the convectionally synthesized samples were characterized by a major absorption band at around 1001 cm^{-1} (Table 5). The lack of adjacent bands at around 1160 and 1082 cm^{-1} in the latter case suggested that the silication by convectional heating was more significant for the damaging of starch macrostructure than the microwave irradiation. Additionally, the shift of the predominant band at around 1000 cm^{-1} towards a higher wave number, regardless the mode of silication, could indicate that there were more C–O–Si and Si–O–Si bonds in microwave and convectionally designed products, respectively. In all the spectra, there was an additional peak at around 450 cm^{-1} assigned to the bending vibrations of Si–O–Si bridging group. This band was absent in the spectrum of native starch.

Table 4
Band assignment in the FT-IR spectra of potato starch and sodium metasilicate.

Sample	Position in cm^{-1} and intensity[a]	Band assignment
Native potato starch	3440 s	ν_{OH} intramolecular hydrogen bond
	2928 m	ν_{CH}
	1648 w	$\nu_{C=O}$, δ_{OH} polymer bound water
	1450 m	
	1432 m	$\delta_{OH,}$ δ_{CH}
	1377 m	$\delta_{OH,}$ δ_{CH}
	1162 s	$\delta_{OH,}$
	1082 s	δ_{C-O-C}, glycosidic linkage
	995 vs	δ_{C-OH}
	929 m	δ_{C-O-C} glycosidic linkage
	859 w	ν_{C-O-C} glycosidic linkage
	765 w	
Sodium metasilicate pentahydrate	3410 s	ν_{X-OH} (X = Si, H)
	2975 m	
	2317 vw	
	1636 w	δ_{HOH}
	1448 s	
	1120m	$\nu_{Si-O-Si}$
	985 s	ν_{SiO} of Si-O$^-$Na$^+$
	866 m	ν_{Si-O} of Si-OH
	838 m	δ_{Si-OH}
	777 w	$\nu_{Si-O-Si}$
	714w	
	636 w	$\delta_{Si-O-Si}$
	459 s	$\delta_{Si-O-Si}$, δ_{O-Si-O}

[a] Abbreviations are related to the band intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Due to electron transfer to the adjacent bridging oxygen atoms, the silicon atom of hydrated metasilicate had large positive charge which made it an active side for the nucleophilic attack from the hydroxyl groups of the D-glucose units of starch, resulting in silication of starch. When starch and sodium metasilicate were taken in the 1:0.05 and 1:0.1 proportions, they could react with an involvement of the silicate moiety and one of the hydroxyl group of the D-glucose units. In that manner a product of monosilication would be formed. Relatively high temperature of decomposition in this case, higher for convectionally rather than microwave-synthesized samples, was attributed to the lower amount of the hydroxyl groups remaining in the starch molecules after silication. When the larger doses of silicating agent were used, they could react intermolecularly with an involvement of two hydroxyl groups yielding a product of crosslinking esterification. Sodium hydroxide formed in such reaction subsequently reacted with one of the hydroxyl groups of the D-glucose units to give sodium starchate (Tomasik & Schilling, 2004, and references therein) and the water molecule. The more sodium metasilicate was used, more hydroxyl groups of the D-glucose units turned into the sodium alkoxide groups, and more water was evolved. A decrease in temperature of the starch decomposition as the silication progressed was connected just with the rising water content. Because of the susceptibility of the Si–O–Si bonds to the water attack, the liberated water could subsequently be incorporated into the product (see Table 3). Wu (1979) found that water was tightly bound in hydrated silicate if the silanols were highly hydrogen-bonded. FT-IR studies confirmed the presence of so bound water in the spectra of starch silicated with the highest doses of metasilicate. An increase in temperature of decomposition when the highest amount of metasilcate was applied, was attributed to the hydrogen bond interactions between silanols and the hydroxyl groups of the D-glucose units, as well as to the crosslinking silication. Based on the shape of bands in the FT-IR spectra, silylation involved formation of the C–O–SiO$_2$Na moieties in the products from the microwave irradiaton, and the Si–O–Si bridges in the products from convectional heating.

3.3. Characterization of silicated starch

3.3.1. X-ray diffraction patterns

Fig. 9 presents diffractograms of potato starch prior and after the microwave irradiation for 30 min at 450 W, of sodium metasilicate pentahydrate, as well as of representative silicated starch samples obtained in the same microwave irradiation conditions. The native B-type crystalline structure of potato starch, characterized by a sharp intense peak at 17.0° 2θ angle and further peaks at 5.8°, 14.9°, 19.6°, 22.2°, 24.0°

Table 5
FT-IR spectra characteristics of starch silication products obtained by convectional heating or microwave irradiation.

Sample	Band position in cm^{-1} and intensity[a]											
Potato starch												
Convectionally heated												
100 °C 120 min	1648 w	1459 m	1375 m	1161 s	1082 s	–	984 vs	927 m	858 w	604 w	574 w	
Microwave irradiated												
450 W 30 min	1637 w	1465 m	1370 m	1162 s	1081 s	–	976 vs	923 m	855 w	594 w	572 w	
800 W 5 min	1648 w	1465 m	1374 m	1160 s	1082 s		981 vs	925 m	858 w	600 w	572 w	
Sodium metasilicate												
Microwave irradiated												
450 W 30 min	–	1450 w		–	–	1028 vw	969 vw	894 w	879 w	–	589 w	417 vs
800 W 5 min	–	1445 w		1173 w	1124 w	–	989 w	–	837 m	777 m	633 w	458 s
Potato starch:sodium metasilicate												
1:0.05												
Convectional heating												
100 °C 120 min	1653 w	1465 m	1374 w	1162 s	1083 s	–	978 vs	924 m	858 w	601 w	573 w	–
Microwave irradiation												
450 W 30 min	1647 w	1465 m	1375 w	1162 s	1081 s	–	979 vs	926 m	859 w	598 w	573 w	–
800 W 5 min	1653 w	1465 m	1380 w	1161 s	1081 s	–	982 vs	926 m	859 w	601 w	573 w	–
1:0.1												
Convectional heating												
100 °C 120 min	1654 w	1473 m	1370 w	1159 s	1085 s	–	982 vs	926 m	856 w	599 w	575 w	–
Microwave irradiation												
450 W 30 min	1653 w	1472 m	1370 w	1161 s	1082 s	–	991 vs	930 m	860 w	605 w	577 w	–
800 W 5 min	1649 w	1466 m	1383 w	1160 s	1081 s	–	987 vs	930 m	857 w	606 w	573 w	–
1:0.25												
Convectional heating												
100 °C 120 min	1654 w	1466 w	1378 w	1163 s	1085 s	1008 vs	985 vs	928 m	857 w	603 w	573 w	–
Microwave irradiation												
450 W 30 min	1654 w	1458 w	1379 w	1165 s	1084 s	1019 vs	984 vs	927 m	858 w	605 w	575 w	–
800 W 5 min	1654 w	1466 m	1379 w	1159 s	1082 s	1016 vs	991 vs	924 m	854 w	606 w	574 w	–
1:0.5												
Convectional heating												
100 °C 120 min	1641 w	1465 w	1375 w	1158 m	1081 m	1018 vs	993 vs	927 m	860 w	607 w	580 w	–
Microwave irradiation												
450 W 30 min	1632 w	1437 w	1370 w	1157 m	1083 m	1019 vs	995 vs	934 m	858 w	608 w	578 w	–
800 W 5 min	1637 w	1452 m	1375 w	1158 s	1081 s	1019 vs	1001 vs	929 m	859 w	609 w	579 w	–
1:1												
Convectional heating												
100 °C 120 min	1657 w	1452 w	–	–	–	–	1001 vs	–	883 w	609 w	–	454 m
Microwave irradiation												
450 W 30 min	1637 w	1433 w	1387 w	1157 m	1082 s	1018 vs	1001 vs	938 m	882 w	615 w	578 w	446 m
800 W 5 min	1646 w	1457 m	1383 w	1158 m	1083 s	1018 vs	1001 vs	–	880 w	619 w	582 w	454 m

[a] Abbreviations are related to the band intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

2θ of the medium intensity, was partly lost after both convectional heating and microwave irradiation. On silication, a progressive flattening of X-ray patterns was observed, regardless the mode of silication, and finally, for the samples with the highest dose of metasilicate, only poor outline of two peaks, at around 17° and 30° 2θ, was noticeable. This significant loss

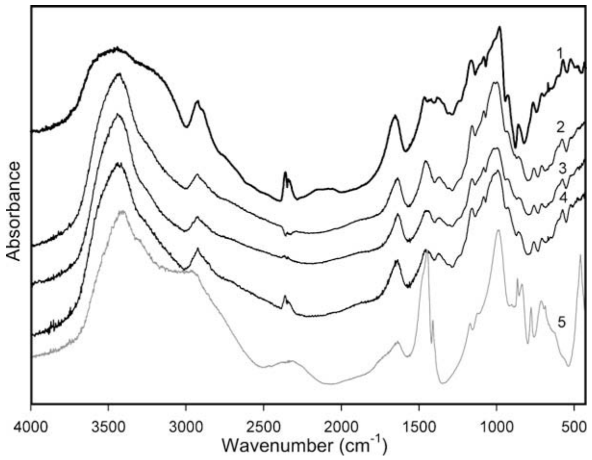

Fig. 7. FT-IR spectra in the range 4000–400 cm^{-1} of potato starch (1), and starch blended with sodium metasilicate (1:0.5) and irradiated by microwaves: 800 W for 5 min (2), 450 W for 30 min (3), and heated convectionally at 100 °C for 120 min (4). Spectrum of sodium metasilicate (5) is shown for comparison. Spectra of plain starch both convectionally heated and microwave irradiated were practically identical.

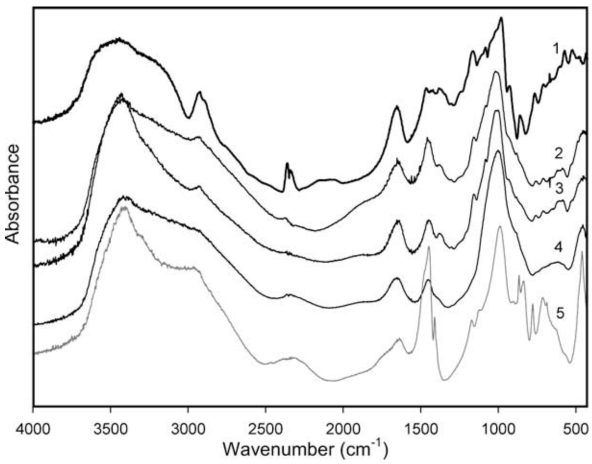

Fig. 8. FT-IR spectra in the range 4000–400 cm^{-1} of potato starch (1), and starch blended with sodium metasilicate (1:1) and irradiated by microwaves: 800 W for 5 min (2), 450 W for 30 min (3), and heated convectionally at 100 °C for 120 min (4). Spectrum of sodium metasilicate (5) is shown for comparison.

of crystallinity of the silicated starch samples was confirmed by the DSC studies.

3.3.2. Thermal properties (DSC analysis)

The melting (phase transition) enthalpy, melting interval and its onset, peak and concluding temperatures for the convectionally heated and microwave irradiated starch were comparable with the corresponding parameters of native starch (Table 6). However, the starch sample irradiated for longer time displayed reduced values of melting temperature and enthalpy. In the case of the silicated starch samples, the DSC parameters could be determined only for these modified with lower doses of metasilicate. For the samples with the lowest dose of silicating agent applied, the recorded values for the melting enthalpy and temperature were lower, and the melting intervals considerably broader, than these of unprocessed starch. Application of another, slightly larger dose, led to a further decrease in these values for starch samples silicated by convectional heating, while for microwave irradiated samples, a decrease in the value of enthalpy accompanied by an increase in melting temperature, were observed. It could imply that in the latter case crosslinking accompanied a progressive expansion of amorphous regions. For the proportions of starch to metasilicate $\geqslant$ 1:0.25 the lack of any clear peak of the phase transition for the silicated samples indicated that the process made the granules completely amorphous.

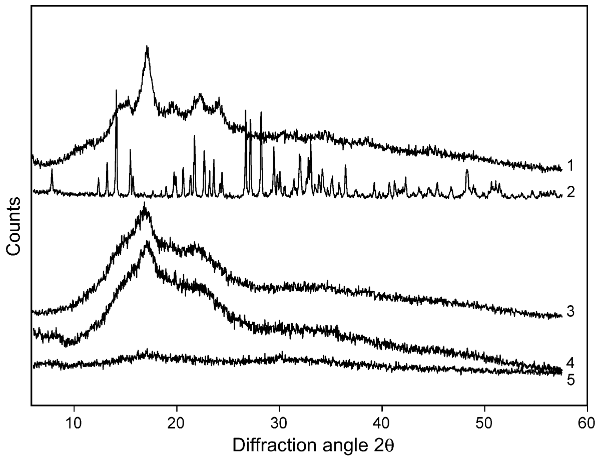

Fig. 9. Powder X-ray diffractograms of native potato starch (1), sodium metasilicate pentahydrate (2), starch after microwave irradiation: 450 W, 30 min (3) and samples from the processing of the 1:0.05 (4) and 1:1 (5) starch:sodium metasilicate blends at the same microwave irradiation conditions.

Table 6
DSC calorimetric parameters for potato starch and its silicated derivatives: onset (T_o), peak (T_p) and conclusion (T_c) melting temperatures, melting temperature interval (ΔT) and melting enthalpy (ΔH). The standard deviation of all estimations did not exceed ±10% of determined value.

Sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔT (°C)	ΔH (J/g)
Native potato starch					
Original	64.0	66.6	70.2	6.2	15.2
Convectionally heated					
100 °C 120 min	63.8	66.4	70.2	6.4	14.6
Microwave irradiated					
450 W 30 min	60.6	64.9	69.5	8.9	10.1
800 W 5 min	63.1	66.0	69.8	6.7	14.9
Potato starch:sodium metasilicate					
1:0.05					
Convectional heating					
100 °C 120 min	50.5	55.4	63.3	12.8	10.8
Microwave irradiation					
450 W 30 min	49.1	53.0	60.1	11.0	9.1
800 W 5 min	49.2	55.1	61.5	12.3	9.7
1:0.1					
Convectional heating					
100 °C 120 min	44.5	49.5	59.0	14.5	7.5
Microwave irradiation					
450 W 30 min	52.3	57.0	64.5	12.2	9.3
800 W 5 min	51.1	55.6	63.1	12.0	7.9

For the potato starch:sodium metasilicate ratios of 1:0.25, 1:0.5 and 1:1 no values could be determined.

Long-time convectional heating, contrary to short-time microwave irradiation, caused a decrease in melting temperature, which could suggest that the degradation predominated over the substitution of the hydroxyl groups of starch (Tomasik, Wiejak, & Pałasiński, 1989). An increase in melting temperature of microwave-synthesized samples suggested formation of the intermolecular

Table 7
Water binding capacity (WBC) and aqueous solubility (AS) of the starch silication products (mean of four measurements ± standard deviation).

Sample	Microwave heating		Convectional heating
	30 min at 450 W	5 min at 800 W	120 min at 100 °C
Water binding capacity (g/g)			
Potato starch	14.63 ± 1.46	17.19 ± 1.59	9.06 ± 4.59
1:0.05	17.45 ± 1.74	17.21 ± 1.70	17.05 ± 1.65
1:0.1	17.96 ± 0.31	15.15 ± 1.36	13.62 ± 1.27
1:0.25	17.25 ± 1.68	15.56 ± 1.54	16.34 ± 0.36
1:0.5	16.88 ± 1.30	8.16 ± 0.81	16.31 ± 1.61
1:1	8.38 ± 0.76	3.91 ± 0.36	12.53 ± 1.20
Aqueous solubility (%)			
Potato starch	6.56 ± 0.30	0.21 ± 0.02	0.06 ± 0.01
1:0.05	6.55 ± 0.10	7.18 ± 0.72	5.24 ± 0.13
1:0.1	12.59 ± 0.27	11.91 ± 0.77	10.21 ± 0.23
1:0.25	17.32 ± 0.86	17.35 ± 0.66	15.73 ± 0.94
1:0.5	31.10 ± 2.51	29.29 ± 2.16	21.40 ± 1.18
1:1	55.38 ± 0.35	67.42 ± 6.81	20.55 ± 2.11

The WBC of the native potato starch was 11.72 (g/g) ± 0.23 and AS 0.41(%) ± 0.14.

bonds and, hence, limited mobility of the chains in the amorphous regions of the starch granules which melted at higher temperature. Further silication would be less selective in respect to the hydroxyl groups, and more damaging to the starch macrostructure, which resulted in a greater aqueous solubility (Table 7).

3.3.3. Solubility and water binding capacity

One could see in Table 7 that the samples with the lowest content of metasilicate were characterized by a low solubility in water (AS), whereas water binding capacity (WBC), for the same samples, was the highest. The samples with the highest content of metasilicate were highly water soluble, while their WBC reached the lowest values.

After the treatment with lower doses of sodium metasilicate, starch became polar, which enhanced WBC and facilitated swelling of starch. WBC decreased as the amount of the silicating agent increased. In this case, keeping of Na^+ ions in the structure of the crosslinked material caused shielding of the silicate anions and preventing from effective anion–anion repulsion. A charge screening effect of the counter ions (Na^+) limited the swelling (Flory, 1953). The smallest WBC, equal to 3.91 g/g, and the largest AS, equal to 67%, were reached for the samples of starch silicated with the largest amount of the silicating agent during the 5 min microwave irradiation at 800 W. For comparison, the convectional heating of the same composition sample resulted in WBC three times higher, and AS three times lower, which would point to the formation of three-dimensional Si–O–Si linking in the product.

Additionally, alkaline degradation of the starch granule after silication could provide an increase in AS and decrease in WBC.

4. Conclusions

(1) Granular potato starch was silicated with sodium metasilicate either by microwave irradiation or by convectional heating.
(2) Products of silication are thermally more stable than the native starch, regardless of the mode of silication.
(3) Water introduced with metasilicate strongly affects the reaction system.
(4) Products of monoesterification and crosslinking esterification are formed.
(5) Increase in the amount of the silicating agent favours crosslinking of starch.
(6) The microwave irradiation and convectional heating produce the C–O–Si and Si–O–Si crosslinks, respectively.
(7) The silication is accompanied by the base-catalyzed destruction of the starch matrix, the more significant for the convectionally heated samples rather than for microwave irradiated material.

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