Carbohydrate Polymers 81 (2010) 599–606

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Microwave-assisted preparation of potato starch silicated with silicic acid

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ARTICLE INFO

Article history:
Received 11 February 2010
Accepted 8 March 2010
Available online 18 March 2010

Keywords:
Microwave-assisted reactions
Potato starch
Silication

ABSTRACT

Application of microwave irradiation for the silication of granular potato starch with silicic acid, and the properties of silicated starch were investigated. Potato starch was esterified on 20 min microwave irradiation of starch with silicic acid, applying the power of 450 or 800 W and, for comparison, on 120 min convectional heating of the reagent blend at 100 °C. The degree of esterification and the reaction efficiency did not depend on the silication mode, but they increased with increasing power of the microwave irradiation. The degree of esterification increased with the reagent ratio. The esterification provided either monoesters or crosslinked esters of retained granularity, insignificantly disrupted crystallinity, and high hydrophobicity. An increased dose of silicic acid in the reaction mixtures provided thermally more stable crosslinked esters.

1. Introduction

There has been an increasing interest in microwave irradiation as an energy source providing fast and uniform heating in the bulk, better selectivity in choosing the reaction pathway and, hence, forming less by-products, and increasing the reaction rate (Kappe & Dallinger, 2009). Among examples of the successful applications of the microwave irradiation to chemical modifications of starch are the solid state esterification with inorganic acids, their salts, anhydrides and oxides, e.g. with sodium phosphates and phosphorous acid (Lewandowicz et al., 2000), with sodium trimetaphosphate (Mao, Wang, Meng, Zhang, Zheng, 2006), with magnesium hydrogen sulfate (Staroszczyk & Tomasik, 2005), with sodium selenate and selenite (Staroszczyk, Tomasik, Janas, & Poreda, 2007), with sulfur trioxide (Staroszczyk, Fiedorowicz, Zhong, Janas, & Tomasik, 2007), with borax and boric acid (Staroszczyk, 2009a), with sodium metasilicate (Staroszczyk, 2009b), and with sodium tetrahydroxozincate (Staroszczyk & Janas, 2010). Usually such modifications produced so-called anionic starches as on their dissociation a negative charge if left on them.

Anionic properties of polysaccharides are essential for intermolecular interactions with other macromolecules, for instance with proteins (Lii, Chen, Lu, & Tomasik, 2003a,b; Lii, Liaw, Lai, & Tomasik, 2002; Lii, Liaw, & Tomasik, 2003; Lii, Tomasik, Zaleska, Liaw & Lai, 2002; Lii, Zaleska, & Tomasik, 2002; Najgebauer, Grega, Sady, & Tomasik, 2003; Najgebauer, Grega, Sady, & Tomasik, 2004; Rutiaga et al., 2005; Tolstoguzov, 1986; Zaleska, Ring, & Tomasik, 2000; Zaleska, Ring, & Tomasik, 2001a,b; Zaleska, Tomasik, & Lii, 2002). The resulting complexes have been considered as biodegradable materials.

Unfortunately, due to their hydrophilic nature, biodegradable plastics which contain such anionic polysaccharide components, exhibit worse barrier properties against water vapor and worse mechanical properties, than petroleum-derived plastics. In order to improve such kind of plastics, studies have been carried out on the modification of one of their components, i.e. either polysaccharide or protein compounds (Bélard, Dole, & Avérous, 2005; Yu, Dean, & Li, 2006; Zhao, Torley, & Halley, 2008).

Recently, natural biopolymers have been filled with layered silicates to improve their functional properties while retaining their biodegradability (Namazi, Mosadegh, & Dadkhah, 2009; Park, Lee, Park, Cho, & Ha, 2003; Rhim & Ng, 2007; Tang, Alavi, & Herald, 2008; Wilhelm, Sierakowski, Souza, & Wypych, 2003). Silylated starches have been tested as thermoplastics and flocculants in the production of beet sugar (Tomasik & Schilling, 2004). They might be considered as environmentally friendly components of biodegradable materials of enhanced hydrophobicity.

In this study, instead of sodium metasilicate (Staroszczyk, 2009b), silicic acid has been used for the synthesis of starch silicates. Such anionic esters of starch could find applications as potential components of biodegradable materials of improved functional properties.

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doi:10.1016/j.carbpol.2010.03.017

2. Experimental

2.1. Preparation method

Native potato starch (13% moisture) isolated in Potato Enterprise in Łomża (Poland) was blended with powdered silicic acid hydrate (purity ≥ 99.0%) from Fluka, at 1:0.1, 1:0.5 and 1:1 (mole D-glucose unit/mole silicic acid) ratio. Thoroughly homogenized blend (2 g) was placed in a microwave oven (Samsung M1711N) and irradiated for 20 min at either 450 or 800 W. For comparison, all samples were convectionally heated for 120 min in an LG MC-8084 NLC oven at 100 °C. After the reaction had been completed, the products were shaken vigorously with 25% aq. ammonia (20 cm^3) in order to remove non-reacted silicic acid, followed by drying at 30 °C until ammonia had evaporated.

2.2. Determination of silicon

The samples (200 or 400 mg) were decomposed with concentrated nitric (d 1.5) and concentrated sulfuric (d 1.84) acids (2:3 mixture), and the acid solution (10 cm^3) was gently refluxed until the brown color ceased. In order to separate silica as an insoluble $SiO_2{\cdot}xH_2O$, 70% perchloric acid (10 cm^3) was added and the solution was heated in an evaporating dish covered with watch glass until dense fumes appeared. After cooling, concentrated hydrochloric acid (10 cm^3) and distilled water (200 cm^3) were added. Then the mixture was brought to boiling, and left overnight for cooling. The precipitate was filtered off, parched in a platinum crucible at 1000–1100 °C and the residue was treated with 48% hydrofluoric acid (15 cm^3). The resulting SiF_4 was evaporated, and the crucible was parched at 1000–1100 °C. The silicon content in the sample was calculated from Eq. (1):

$$W(\%) = 0.4674 \times \frac{m_1 - m_2}{m} \times 100\% \qquad (1)$$

where 0.4674 was a factor converting SiO_2 into Si, m_1 and m_2 were the mass of crucible with precipitate and the mass of crucible after removing SiF_4 and parching (mg), respectively, and m was the initial mass of the sample (200 or 400 mg). Estimations were run in duplicates.

2.3. Thermogravimetric analysis (TG and DTG)

Thermogravimetric analysis was performed with a TG/SDTA Mettler-Toledo 851^e apparatus located in Regional Laboratory of Physicochemical Analyses and Structural Research in Cracow (Poland). The samples (∼30 mg) were heated in open alumina crucibles in the air (80 cm^3/min), within temperature range of 25–600 °C, at a heating rate of 10 °C/min.

2.4. Fourier transformation infrared spectroscopy (FT-IR)

The FTIR spectra of samples (3 mg) in KBr (300 mg) discs were recorded in the range of 4000–500 cm^{-1} at the 4 cm^{-1} resolution, using the Perkin Elmer Spectrum BX spectrophotometer.

2.5. 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. Then they were scanned, at the rate of 6 °C/min, from 20 to 90 °C. An instrument, self-assembled at the Department of Chemistry and Physics of the University of Agriculture in Cracow (Poland) was used. A water filled pan served as a reference. Analyses were run in triplicates.

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. Scanning Electron Microscopy (SEM)

Granule morphology of starch samples was examined by means of an 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.

2.8. Aqueous solubility and water binding capacity

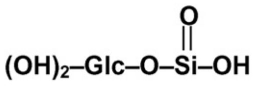
Aqueous solubility (AS) and water binding capacity (WBC) at room temperature were estimated according to Richter, Augustat, and Schierbaum (1968). Estimations were repeated ten times for each sample.

3. Results and discussion

Silicated starch derivatives were formed on either microwave irradiation or convectional heating of potato starch blended with silicic acid at various proportions (mole D-glucose unit/mole silicic acid). The results of elemental analysis (Table 1) revealed that the irradiation at 450 W and the convectional heating at 100 °C provided approximately the same results in terms of the degree of esterification (DE), equal to about 0.07, 0.48 and 0.90 for 1:0.1, 1:0.5 and 1:1 starch/silicic acid proportions, respectively, while the irradiation at 800 W was slightly more favourable in this respect and offered products of DE equal to 0.10, 0.50 and 0.90, for respectively the same reagent proportions as above.

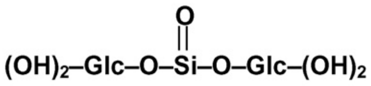
Thus, the application of the microwave irradiation considerably shortened the time of the process, and also improved, to some extent, the reaction efficiency (RE). An increased power of the irradiation contributed to higher DE and RE, however, more significantly when the smaller amount of admixed acid was applied.

Silicic acid, a dibasic acid, could react through an involvement of either one or two of its reactive groups with the hydroxyl groups of the D-glucose units of starch, $(OH)_2\text{–Glc–OH}$, giving either (**1**) or (**2**).



$$(OH)_2\text{–Glc–O–}\overset{\overset{\displaystyle O}{\|}}{Si}\text{–OH}$$

(1)



$$(OH)_2\text{–Glc–O–}\overset{\overset{\displaystyle O}{\|}}{Si}\text{–O–Glc–}(OH)_2$$

(2)

The distinction between both reaction courses, e.g. the formation of either (**1**) or (**2**), was based on the estimation of the amount of water that evolved on esterification, which should be 1 and 0.5 mole per mole of D-glucose unit, respectively. The estimations shown in Table 2 takes into account the loss of water from plain starch and silicic acid on heating in the range of 25–161 °C, and the formerly determined RE (Table 1). As it could see, in the case of the products of the microwave irradiation at 450 W and the convectional heating at 100 °C the estimations fitted structure (**1**) as that predominating when the smaller amount of admixed acid was applied, and structure (**2**) as that prevailing when the larger amount of admixed acid was applied. An increase in the irradiation

Table 1
Determination of degree of esterification in silicated starch.

Starch:silicic acid initial ratio	Microwave irradiated at 450 W				Microwave irradiated at 800 W				Convectionally heated at 100 °C			
	Si in the product (%)		DE[c]	RE[d] (%)	Si in the product (%)		DE	RE (%)	Si in the product (%)		DE	RE (%)
	Calculated[a]	Found[b]			Calculated	Found			Calculated	Found		
1:0.1	1.52	1.12	**0.07**	74	1.52	1.58	**0.10**	100	1.52	1.23	**0.08**	81
1:0.5	6.66	6.36	**0.48**	96	6.66	7.18	**0.50**	100	6.66	6.22	**0.47**	93
1:1	11.52	10.40	0.91	90	11.52	10.53	**0.91**	91	11.52	10.18	**0.88**	88

[a] Assuming 100% reaction yield.
[b] Found amount of Si in silicic acid was 42.57%.
[c] Degree of esterification.
[d] Reaction efficiency calculated on the basis of the ratio calculated and found amount of silicon in the product.

Table 2
Balance of the water loss on starch silication indicating the course of the reaction.

Starch:silicic acid initial ratio	Microwave irradiated at 450 W Weight loss (%)			Microwave irradiated at 800 W Weight loss (%)			Convectionally heated at 100 °C Weight loss (%)		
	Calculated for[a]		Found[b]	Calculated for		Found	Calculated for		Found
	(1)	(2)		(1)	(2)		(1)	(2)	
1:0.1	**10.85**	5.43	10.32	14.66	7.33	10.51	**11.87**	5.94	10.19
1:0.5	**12.85**	6.43	10.13	13.39	6.70	10.30	**12.45**	6.23	12.10
1:1	10.96	**5.48**	6.88	11.08	**5.54**	6.71	10.72	5.36	5.09

[a] For water elimination in case of (1) or (2).
[b] From the thermogram.

power did not provide any clear distinction between the formation of (**1**) and (**2**) in the case when the smaller concentrations of silicon reagent were used. The higher irradiation power appeared more essential for the formation of (**2**) at higher dose of silicic acid.

The thermogram in Fig. 1 demonstrates that the decomposition maximum of native potato starch occurred at 295 °C, and at 600 °C there was the 99.07% weight loss (see also Table 3). Silicic acid did not decompose up to 600 °C, evolving hardly 4.47% water (Fig. 2).

At the first sight, all products of silication were thermally slightly less stable, as they decomposed at about 7 °C lower temperature than the original native starch, regardless of the silication mode applied. However, a closer look at the pattern of the TG lines (Table 4) revealed that the decomposition temperatures of starch silicated with larger amount of admixed acid were higher than those for starch silicated with smaller amount of that acid. It was particularly pronounced for the products of the microwave irradiation at 800 W (Fig. 3). An increase in thermal stability of these products would confirm crosslinking of starch through the esterification with the involvement of two reactive groups of dibasic silicic acid, i.e. the formation of (**2**). The total weight losses of these products, lower by about 30% than that of native starch, together with their considerable lower rates of decomposition, reflected by the slope of the TG line, would also confirm crosslinking esterification.

Table 5 lists the band assignment in the FT-IR spectra of potato starch (Bellon-Maurel, Vallat, & Goffinet, 1995; Cael, Koenig, & Blackwell, 1975; Kizil, Irudayaraj, & Seetharaman, 2002; Sekkal, Dincq, Legrand, & Huvenne, 1995; Wilson & Belton, 1988; Wilson, Goodfellow, & Belton, 1988) and of silicic acid (Neves, Lenza, & Vasconcelos, 2002; Uchino, Sakka, Hotta, & Iwasaki, 1989; Uchino, Sakka, & Iwasaki, 1991). The products of their reaction are spectrally characterized in Table 6.

A decrease in the intensity of the broad band in the region between 3700 and 3000 cm^{-1}, as well as of the bands at 1162 and 995 cm^{-1} (Fig. 4), assigned to the stretching vibrations of the OH group as well as to the bending vibrations of the C–OH bond, respectively, revealed the loss of the OH groups in D-glucose units as the

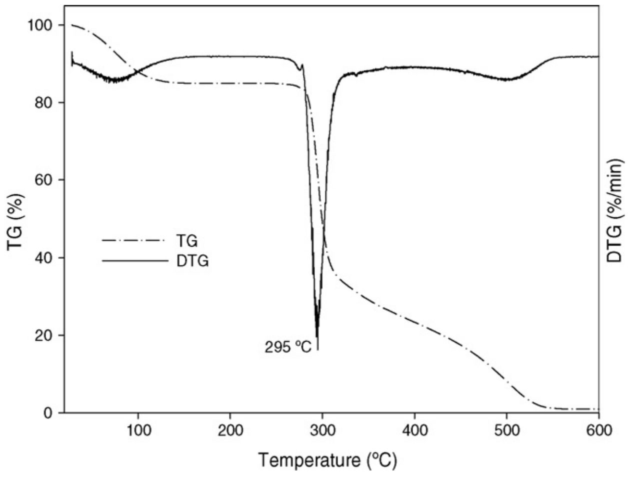


Fig. 1. Thermogram of native potato starch.

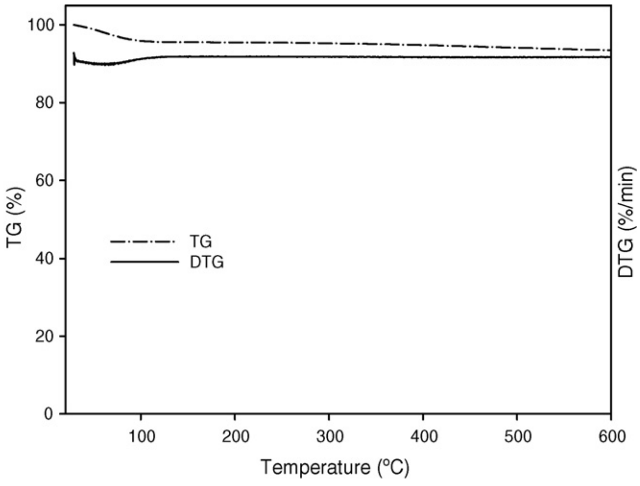


Fig. 2. Thermogram of silicic acid.

Table 3
Thermogravimetric characteristics of potato starch and silicic acid.

Sample	Temperature range (°C)	Weight loss (%)[a]	Slope (tg α)[b]	DTG (°C)
Native potato starch	25–161	15.04		75
	161–352	56.06	1.10	295
	352–600	27.97		
	Total	99.07		
Microwave irradiated at 450 W	25–161	2.50		100
	161–352	63.34	1.23	294
	352–600	33.40		
	Total	99.24		
Microwave irradiated at 800 W	25–161	1.93		95
	161–352	64.99	1.20	294
	352–600	32.14		
	Total	98.73		
Convectionally heated at 100 °C	25–161	4.89	1.22	97
	161–352	62.80		295
	352–600	31.14		
	Total	98.83		
Silicic acid	25–161	4.47		63
	161–352	0.45		
	352–600	1.58		
	Total	6.50		

[a] Weight loss (%) in the specified temperature ranges.
[b] The slope of TG line.

Table 4
Thermogravimetric characteristics of starch silication products.

Starch:silicic acid initial ratio	Temperature range (°C)	Microwave irradiated at 450 W			Microwave irradiated at 800 W			Convectionally heated at 100 °C		
		Weight loss (%)[a]	Slope (tg α)[b]	DTG (°C)	Weight loss (%)	Slope (tg α)	DTG (°C)	Weight loss (%)	Slope (tg α)	DTG (°C)
1:0.1	25–161	10.32		75	10.51		77	10.19		80
	161–352	53.17	0.75	287	52.33	0.74	288	52.76	0.70	285
	352–600	32.62			32.23			32.89		
		(96.11)[c]			(95.07)			(95.84)		
1:0.5	25–161	10.13		75	10.30		75	12.10		73
	161–352	42.89	0.60	284	40.36	0.51	289	39.06	0.50	285
	352–600	32.12			30.19			31.03		
		(85.14)			(80.85)			(82.19)		
1:1	25–161	6.88		78	6.71		76	5.09		78
	161–352	38.29	0.41	288	36.43	0.35	293	34.66	0.32	289
	352–600	32.40			28.03			28.76		
		(77.66)			(71.17)			(68.51)		

[a] Weight loss (%) in the specified temperature ranges.
[b] The slope of TG line.
[c] Data in parenthesis were the overall weight loss values at up to 600 °C.

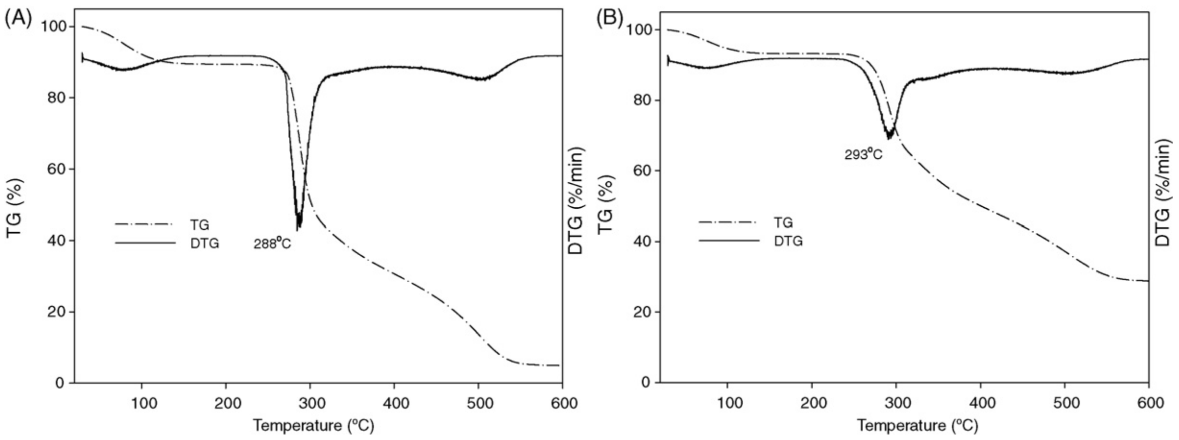


Fig. 3. Thermograms of the reaction products from the microwave irradiation with 800 W of the 1:0.1 (A) and 1:1 (B) starch/silicic acid blends.

Table 5
Band assignment in the FT-IR spectra of potato starch and silicic acid.

Potato starch		Silicic acid	
Position in cm^{-1} and intensity[a]	Band assignment	Position in cm^{-1} and intensity	Band assignment
3440 s	ν_{OH} inter- and intra-molecular H-bond	3450 s	$\nu_{X–OH}$ (X = Si, H)
2928 m	ν_{CH}	1629 w	δ_{HOH}
1648 w	δ_{OH} polymer bound water	1100 vs	$\nu_{Si–O–Si}$
1432 m	δ_{OH}, δ_{CH}	969 w	$\nu_{Si–OH}$
1377 m	δ_{OH}, δ_{CH}	803 w	$\nu_{Si–O–Si}$
1162 s	$\nu_{C–C}$, $\nu_{C–O}$, $\delta_{C–OH}$	477 vs	$\delta_{Si–O–Si}$, $\delta_{O–Si–O}$
1082 s	$\delta_{C–OC}$ α-1,4glycosidic linkage		
995 vs	$\delta_{C–OH}$		
929 m	$\delta_{C–OC}$ α-1,4 glycosidic linkage		
859 w	$\nu_{C–O–C}$ glycosidic linkage		
765 w	$\nu_{C–C}$		

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

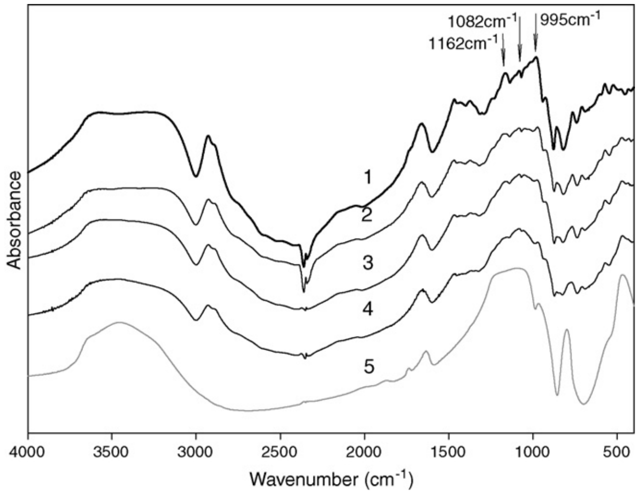


Fig. 4. FT-IR spectra of potato starch (1), and samples from the processing of the 1:1 blends in different conditions: convectional heating at 100 °C (2), microwave irradiation with 450 W (3) and 800 W (4). Spectrum of silicic acid (5) is shown for comparison.

silication process progressed. Simultaneously, an increase in the intensity of the band at 1082 cm^{-1} with an increasing amount of admixed acid could be observed. That band, representing the vibrations of the C–O–C of α-1,4 glycosidic linkage in the starch molecule (Table 5), could also originate from the vibrations of a new bond that formed between silicic acid and starch. The similar band was also observed by Tang, Zou, Xiong, and Tang (2008), who attributed it to the C–O–Si group that formed between nano-silicon dioxide (nano-SiO_2) and corn starch in starch/polyvinyl alcohol/nano-SiO_2 biodegradable blend films prepared by a solution casting method. The formation of the C–O–Si bond in starch silication products could also be reflected by a shift of the band assigned to the bending vibrations of the C–OH bond in starch (995 cm^{-1}) by 5–18 cm^{-1} (Table 6). The energy of that bond decreased, likely due to the formation of the conformational changes of starch to provide silication. It is worth noting that while that band moved towards lower wave numbers, the band assigned to the stretching vibrations of the Si–OH in silicic acid (969 cm^{-1}) shifted towards higher wave numbers, reflecting a new C–O–Si bond. In the spectra of the products silicated with a larger amount of admixed acid, the new band at 477 cm^{-1} could also be observed. This band, corresponding to the bending vibrations of Si–O–Si bond, might indicate that silication involved the formation of the Si–O–Si bridges in the products.

All of these spectral changes confirmed the success of starch esterification by silicic acid. The comparison of the patterns of the spectra in the region between 3700 and 3000 cm^{-1} (Fig. 4) assigned to the stretching vibrations of the inter- and intra-molecular hydrogen bond in starch (Table 5) revealed that although the width of

Table 6
FT–IR spectra characteristics starch silication products obtained by microwave irradiation or convectional heating.

Sample	Band position in cm^{-1}						
Potato starch:silicic acid =1:0.1							
Microwave irradiated at 450 W	1162	1082	–	995	929	859	–
Microwave irradiated at 800 W	1162	1082	1050	990	929	859	–
Convectionally heated at 100 °C	1162	1082	–	995	929	859	–
Potato starch:silicic acid =1:0.5							
Microwave irradiated at 450 W	1162	1082	1050	990	929	859	477
Microwave irradiated at 800 W	1162	1082	1062	979	929	859	477
Convectionally heated at 100 °C	1162	1082	1050	985	929	859	477
Potato starch:silicic acid =1:1							
Microwave irradiated at 450 W	1162	1082	1050	979	929	859	477
Microwave irradiated at 800 W	1162	1082	1062	977	929	859	477
Convectionally heated at 100 °C	1162	1082	1050	977	929	859	477

Table 7
DSC calorimetric parameters: phase transition enthalpy (ΔH) and its onset (T_o), peak (T_p) and conclusion (T_c) temperatures of potato starch and its silicated derivatives. The standard deviation of all estimations did not exceed ±10% of determined value.

Sample	Microwave irradiated at 450 W				Microwave irradiated at 800 W				Convectionally heated at 100 °C			
	T_o (°C)	T_P (°C)	T_c (°C)	ΔH (J/g)	T_o (°C)	T_P (°C)	T_c (°C)	ΔH (J/g)	T_o (°C)	T_P (°C)	T_c (°C)	ΔH (J/g)
Starch[a]	55.3	62.3	70.4	14.7	52.0	63.1	79.2	2.5	55.7	63.3	71.0	16.4
1:0.1[b]	55.8	61.8	69.3	12.0	54.5	61.2	69.2	10.6	56.8	62.6	70.0	13.1
1:0.5	56.0	61.6	68.6	9.5	55.2	61.5	68.6	8.8	57.1	62.6	69.5	11.7
1:1	55.3	61.9	68.3	7.9	54.1	60.4	67.8	8.1	55.5	62.0	68.6	8.6

[a] T_o, T_p, T_c and ΔH of native starch was 58.6 °C, 64.8 °C, 71.0 °C and 16.5 J/g, respectively.
[b] Starch:silicic acid initial ratio (mole D-glucose unit/mole silicic acid).

that band after silication remained unchanged, the absorption patterns of the products slightly differed from each other and from the spectrum of native starch. Thus, it was likely that the hydrogen bonds in starch underwent rearrangement during silication, affecting changes in the molecular order and in the degree of starch crystallinity. Such changes were also supported by the development of a new peak at about 1050 cm^{-1}, characteristic of a more organised part of starch (Smits, Ruhnau, Vliegenthart, van Soest, 1998), in all the spectra of starch derivatives in which the amount of silicic acid was increased.

The X-ray diffractometry and thermal analysis (DSC) proved that the changes in the crystallinity of silicated starches occurred. As it could be seen from the X-ray patterns (Fig. 5), while starch granules lost their semi-crystalline character after the exposition of starch to microwaves in the absence of the silicon reagent, silicated starches revealed symptoms of crystallinity and developed a peak centred around 22.3 2θ, resembling that for silicic acid, but the present peak was sharper.

Unlike the convectional heating, the microwave irradiation of starch decreased the phase transition enthalpy (ΔH), and had a strong effect dependent on the irradiation power applied (Table 7). Changes in the granule structure induced by the irradiation of starch at 450 W weakened the inter- and intra-molecular hydrogen bonds, facilitating thus the diffusion of water inside the granules

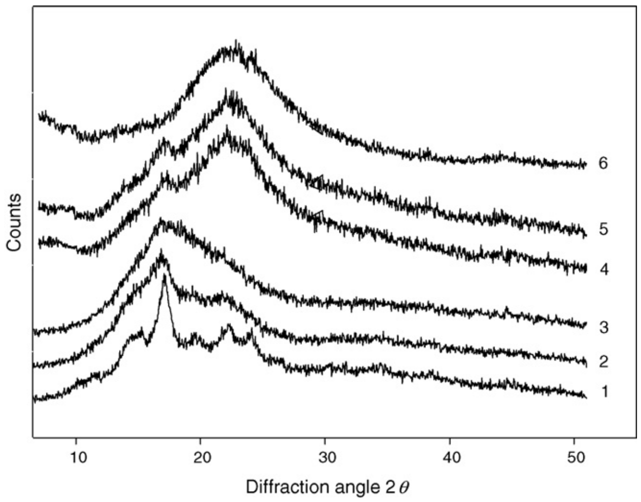


Fig. 5. Powder X-ray diffractograms of potato starch prior (1) and after microwave irradiation at 450 W (2) and 800 W (3) as well as the silication products resulting from microwave irradiation at 450 W (4) and 800 W (5). Diffractogram of silicic acid (6) is added for comparison.

Table 8
Water binding capacity (WBC) and aqueous solubility (AS) of potato starch and its silicated derivatives. The standard deviation of all estimations did not exceed ±10% of determined value.

Sample	Microwave irradiated at 450 W		Microwave irradiated at 800 W		Convectionally heated at 100 °C	
	WBC (g/g)	AS (%)	WBC (g/g)	AS (%)	WBC (g/g)	AS (%)
Starch[a]	130.15	0.05	1.44	38.55	63.35	0.06
1:0.1[b]	18.87	0.02	10.59	1.91	15.82	0.04
1:0.5	16.66	0.02	11.52	1.71	12.48	0.02
1:1	24.41	0.02	21.33	0.09	24.77	0.02

[a] The WBC of native starch was 9.41 (g/g) and AS 0.02 (%).
[b] Starch:silicic acid initial ratio (mole D-glucose unit/mole silicic acid).

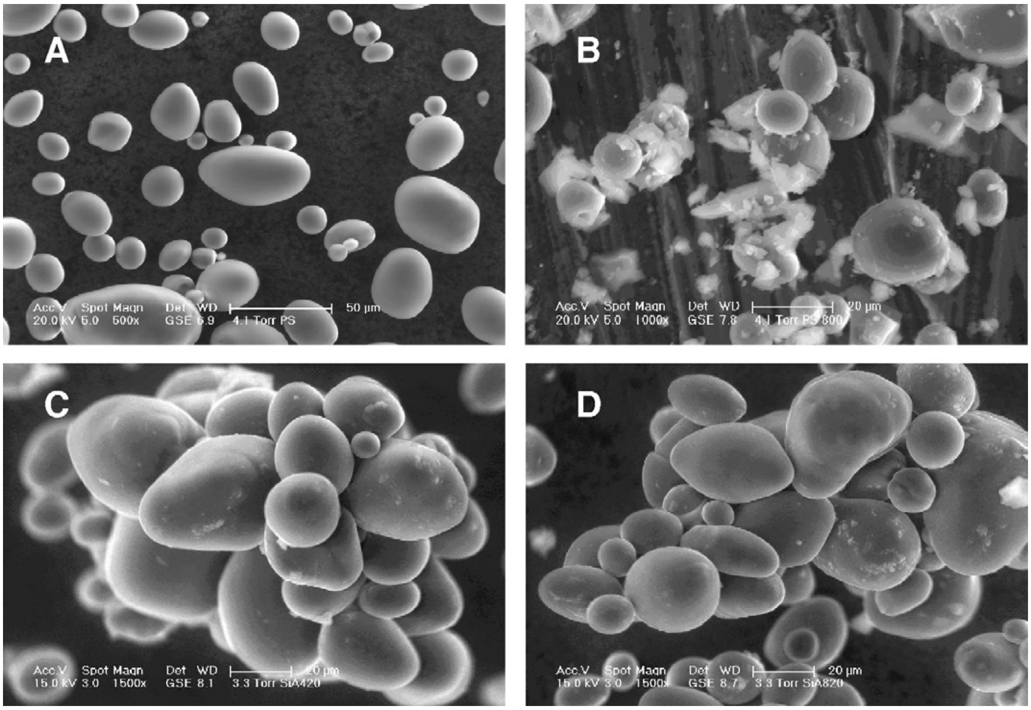


Fig. 6. Scanning electron micrographs of starch granules: native (A), irradiated at 800 W without silicic acid (B), and silicated with silicic acid (1:1 starch/silicic acid) at 450 W (C) and 800 W (D).

and enhancing the water binding capacity (WBC) of starch. An increase in the power of irradiation made the granules more amorphous, facilitating the solubility in water (AS), but suppressing WBC (Table 8).

The silication of starch caused a decrease in the ΔH values with respect to that observed for native starch. However, in the case of the products of microwave irradiation at 800 W, a significant increase in ΔH compared to that of the control sample suggested the crosslinking of starch. On one hand the inter- and intra-molecular hydrogen bonds were weakened on the silication, thus the granules could absorb water more easily (Table 7), but on the other hand, the granules held together by crosslinking became less water soluble. It provided the also granule agglomeration (Fig. 6).

The morphological changes of granules of silicated starch are presented in Fig. 6. The microwave irradiation of starch without silicic acid led to the deterioration of granular structure (Fig. 6B), whilst its silication at 450 and 800 W inhibited the granularity, in spite of the granule swelling (Fig. 6C and D).

4. Conclusions

Microwave-assisted silication of potato starch with silicic acid was successful. The application of the microwave irradiation gave products of approximately the same degree of esterification as convectional heating, but the reaction time was considerably shorter, and the reaction efficiency improved. The increased microwave power was more efficient for the process. The silication resulted in the formation of either monoesters or diesters, that is, crosslinked esters, depending on the starch: silicic acid ratio. The increased amount of admixed acid influenced the formation of thermally more stable crosslinked esters. The silication only insignificantly disrupted starch crystallinity, but retained starch granularity. The aqueous solubility of silicated starch was very low, thus the silication offered hydrophobic products.

Acknowledgements

This study was supported by the Polish Ministry of Science and Higher Education under Grant N N 312 205436.

The authors are grateful to Prof. Dr. Piotr Tomasik from the University of Agriculture in Cracow, Poland, for critical review of this manuscript.

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