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Microwave-assisted synthesis of zinc derivatives of potato starch

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ABSTRACT

Zincatated potato starch was prepared in a solid-state, microwave-assisted reaction using generated *in situ* sodium tetrahydroxozincate [$Na_2Zn(OH)_4$]. For comparison, zincatation of starch was also carried out on convectional heating. Depending on the irradiation conditions, the products of either mono- or crosslinking esterification were formed. Higher power applied at shorter exposition offered products of monoesterification, and the lower power at longer exposition favoured crosslinking of starch. The microwave-assisted processes were faster than these proceeding on convectional heating. The reaction time was reduced from 120 to 30 min. The crystallinity of resulting products gradually ceased with increased concentration of introduced zincate but their granularity was retained independently of that concentration. The thermal stability of the products was slightly lower than that of native starch. Already reaction product prepared with the smallest dose of zincate had significantly decreased melting temperature and melting enthalpy and, simultaneously, increased aqueous solubility as well as water binding capacity compared to non-processed starch.

1. Introduction

The chemical reactivity of starch is controlled, among others, by the reactivity of the hydroxyl groups of its D-glucose units. These hydroxyl groups react as the hydroxyl groups of primary and secondary alcohols, that is, they undergo oxidation, etherification, esterification and form metal salts. An essential difference between the reactivity of these groups in common alcohols and in starch results from a spare solubility of starch and its reaction products. Thus, several reversible reactions of common alcohols, for instance the metal salt and esterification, becomes irreversible in starch.

Starch can esterify organic and inorganic acids. When dibasic inorganic and organic acids are esterified, monoesterification provides anionic products (Tomasik & Schilling, 2004) evoking considerable interest for their ability to adhere to materials of cationic character and being proton donors, for instance, cotton and proteins. The resulting sizes and biodegradable materials enjoy with a wide potential applications, for instance, biodegradable packaging materials of improved functional properties (Lacroix, 2009, chap. 13 and references therein). Anionic starch, on forming complexes or crosslinks with other partners, can contribute to the improvement of mechanical properties of the composites (Rutiaga et al., 2005). Esters of starch with inorganic acids, for instance boric (Staroszczyk, 2009a), selenous and selenic (Staroszczyk, Tomasik, Janas, & Poreda, 2007) acids, can be considered as carriers of these elements for biological applications.

Recently, some attention has been paid to zinc mono- and disaccharides (Bandwar, Giralt, Hidalgo, & Rao, 1996), as well as starch (Tomasik & Schilling, 2004, and references therein; Woo, Bassi, Maningat, Ganjyal, & Zhao, 2006) because zinc is an essential trace element that possesses antioxidant properties, necessary for sustaining all animal lives. For their biological significance Zn^{2+}-saccharide complexes could be used as carriers of zinc for supplementation of food, as well as cosmetic and pharmaceutical compositions (Bandwar et al., 1996). These properties prompted us towards esterification of zinc acid used in form of sodium tetrahydroxozincate [$Na_2Zn(OH)_4$] with starch.

There is a number of successful applications of the microwave irradiation to chemical modifications of starch. Such kind heating provided facile acetylation (Shogren & Biswas, 2006), succinylation (Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005), maleation (Xing, Zhang, Ju, & Yang, 2006), phosphorylation (Lewandowicz et al., 2000; Mao, Wang, Meng, Zhang, & Zheng, 2006), sulphation (Staroszczyk, Fiedorowicz, Zhong, Janas, & Tomasik, 2007), magnesium sulphation (Staroszczyk & Tomasik, 2005), selenation (Staroszczyk et al., 2007), boration (Staroszczyk, 2009a) and silication of starch (Staroszczyk, 2009b). It should be underlined that such reactions could be carried out in the solid state and the same approach was applied in this study.

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2. Materials and methods

2.1. Materials

Native potato starch (13% moisture) was isolated in Potato Enterprise in Łomża, Poland. Zinc oxide was purchased from Sigma–Aldrich and sodium hydroxide was the product of P.P.H. Stanlab s.j. (Lublin, Poland).

2.2. Preparation of sodium zincate in situ

Zinc oxide (5.82 g) was weighed into a clean evaporating dish and excess sodium hydroxide (40 cm^3 of 40% aqueous solution) was added. The mixture was heated gently on a hot plate to form after 30 min a clear solution. Colourless crystals of sodium tetrahydroxozincate isolated on evaporation were dried under vacuum and used without further purification.

2.3. Preparation of starch zincate

Potato starch was blended with sodium zincate at proportions 1:0.05, 1:0.1, 1:0.25, and 1:0.5 (mole D-glucose unit/mole zinc compound) and thoroughly homogenized in an agate mortar. Final blends (2 g) were irradiated in a Samsung M1711N microwave oven either for 30 min at 450 W or for 1 min at 700 W. For comparison, all samples were convectionally heated in a LG MC-8084 NLC oven for 120 min at 100 °C. All reaction products without any purification were stored in tightly closed vessels.

2.4. Thermal analysis (TG, DTG, DTA)

Samples (100 mg) were heated in corundum crucibles up to 1000 °C at the 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.

2.5. 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, WI, USA) spectrophotometer.

2.6. Differential scanning calorimetry (DSC)

The samples (approximately 8 mg) were sealed in a 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 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.

2.7. 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 Cu K_α radiation of wavelength of 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.

2.8. Scanning electron microscopy (SEM)

Granule morphology of starch samples was investigated by using 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.

2.9. Aqueous solubility and water binding capasity

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

None of the microscopic examinations of the zincatated products revealed any objects which could be identified either as non-reacted zincate or products of its decomposition. Therefore, the reaction products were analyzed under the assumption that zincate completely reacted with starch.

After zincatation the shape of starch granules was retained (Fig. 1). The reaction with lower doses of zincate left most of granules smooth but the higher doses of zincate produced granules with a rough surface, protuberances, pores and grooves.

Zinc oxide dissolved in dilute alkaline solutions could exist as either $Zn(OH)_2$, $Zn(OH)_3^-$ or $Zn(OH)_4^{2-}$ (Dirkse, Postmus, & Vandenbosch, 1954; Smith, Bell, Borodin, & Jaffe, 2001; Stahl, Niewa, & Jacobs, 1999). In concentrated alkaline solutions, the $Zn(OH)_4^{2-}$ complex ion predominated (Dirkse et al., 1954; Fordyce & Baum, 1965; Pandaya, Russel, McBreen, & O'Grady, 1995). The following simplified equations for its formation were accepted:

$$ZnO + OH^- + H_2O \rightarrow Zn(OH)_3^- \quad (1)$$

$$ZnO + 2OH^- + H_2O \rightarrow Zn(OH)_4^{2-} \quad (2)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO_2^{2-} + 2H_2O \quad (3)$$

Sodium zincate prepared *in situ* decomposed thermally in two steps as shown in Fig. 2. These steps could correspond to transformations providing sodium oxodihydroxozincate (4) and zinc oxide (5), respectively (Smith et al., 2001) with a total weight

$$Na_2Zn(OH)_4 \rightarrow Na_2ZnO(OH)_2 + H_2O \quad (4)$$

$$Na_2ZnO(OH)_2 \rightarrow ZnO + Na_2O + H_2O \quad (5)$$

loss of 18.64% (Table 1).

The involvement of reaction (4) was confirmed by the 9.96% weight loss perfectly fitting calculated value of 10.03%. In the second step 8.86% weight loss was observed. This result did not fit calculations (11.15%).

Native starch lost sorbed water at 96 °C, followed by one decomposition step centered at 277 °C (Fig. 3) with a weight loss of 40.2% in the range of 176–491 °C (Table 1). There were no distinct differences in the shapes of thermograms of starch samples zincatated under different conditions. Fig. 4 demonstrates thermograms of starch zincatated in the microwave-assisted reaction (450 W, 30 min) with different doses of the zincate. Decomposition of native and zincatated starch with the lowest dose of zincate (proportion of 1:0.05) proceeded in one step. For products zincatated with higher doses of zincate, i.e. reacted in starch:zincate proportions of 1:0.1, 1:0.25 and 1:0.5, at least two decomposition steps, represented by two endothermic peaks seen on the DTG curves, were observed. The first step, represented by the peak appearing in the range of 176–491 °C, at temperature slightly lower than that of decomposition of native starch and its zincatated

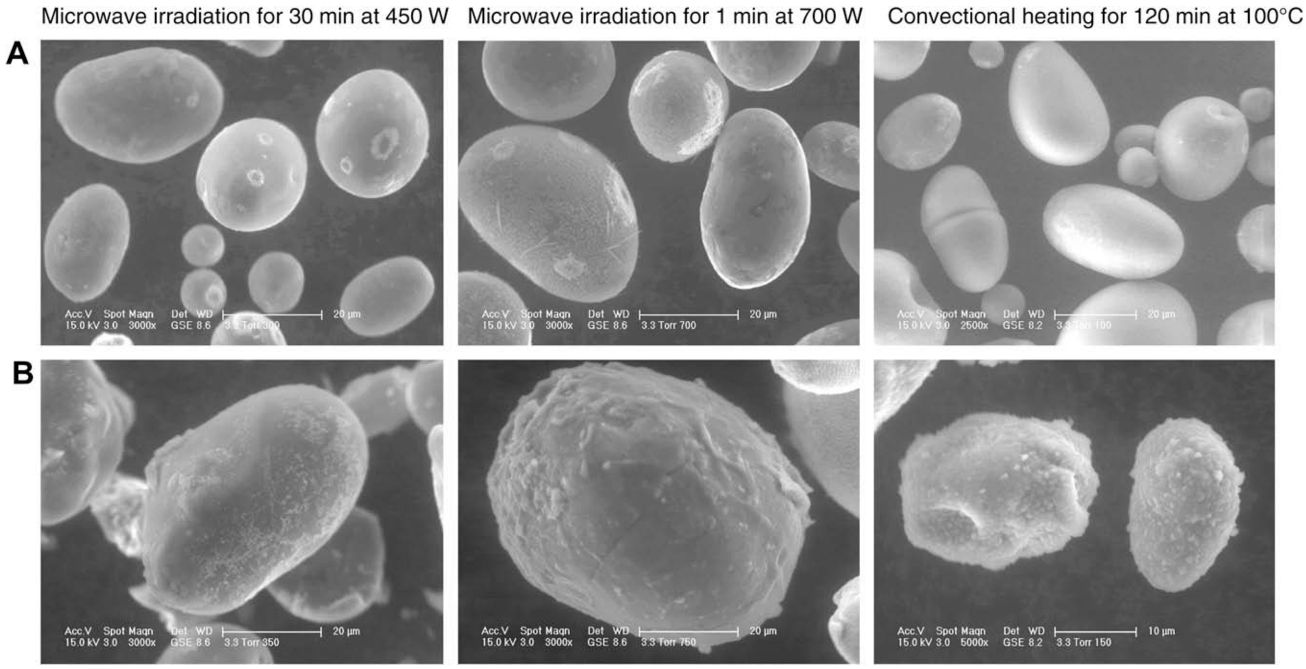


Fig. 1. The scanning electron micrographs of starch zincatated on the microwave irradiation and convectional heating of 1:0.05 (A) and 1:0.5 (B) blend.

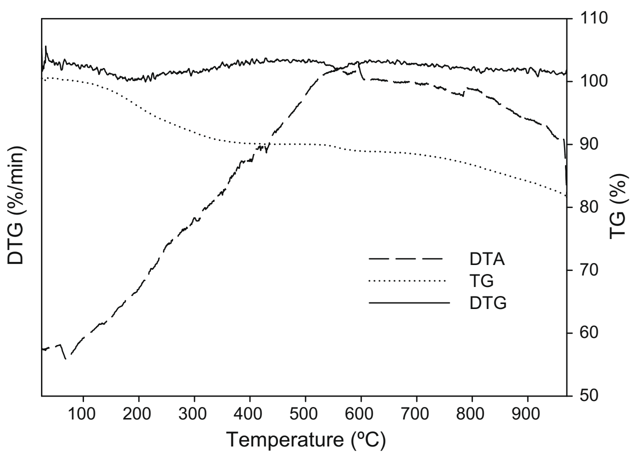


Fig. 2. Thermogram of sodium tetrahydroxozincate.

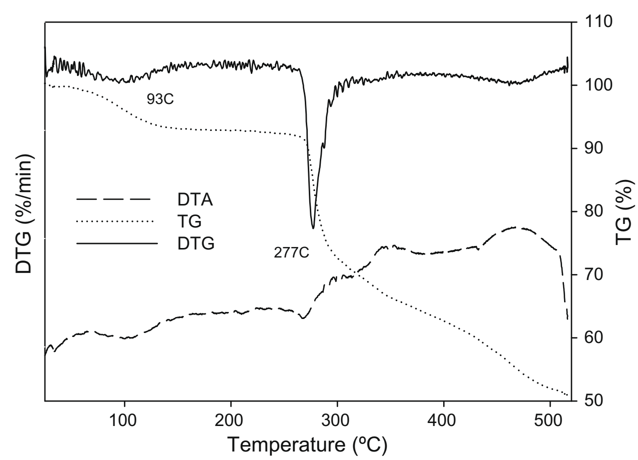


Fig. 3. Thermogram of native potato starch.

derivative of the lowest degree of substitution, was associated with decomposition of zincatated starch. The second step, represented by the peak in the range of either 491–650 °C or 650–970 °C, for the samples resulting from processing of 1:0.1 and 1:0.25 or 1:0.5 blends, respectively (see also Table 2) could reflect further decomposition of carbonizate in the presence of a zinc containing residue, for instance, zinc oxide. The zincatation of starch resulted in decrease in decomposition temperature of the products in respect to decomposition of plain starch and that decrease was more remarkable in more zincatated starches.

As revealed by the slope of the TG line, zincatated starch decomposed less readily than starch, and the weight loss associated with its decomposition (measured in the range of 176–491 °C) gradually decreased by approximately the same magnitude, independently of the mode of zincatation (Table 2). Such changes of the thermal properties could suggest that zincatation might result in crosslinking of starch.

Since there were considerable resemblances between decomposition temperatures, the weight losses, and the decomposition rates of starch zincatated on microwave irradiation (450 W, 30 min) and convectional heating, it was likely that both processes provided similar products but microwave-assisted process was by

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

Sample	Temperature range (°C)	Weight loss[a] (%)	Slope[b] (tg α)	DTG (°C)
Potato starch	25–176	7.02		96
	176–491	40.20		277
	491–650	2.66	1.11	
	650–970	1.18		
	Total	51.06		
Sodium zincate	25–176	2.61		
	176–491	7.35		196
	491–650	1.57		561
	650–970	7.11		
	Total	18.64		

[a] The weight loss [%] within the specified temperature range.
[b] The slope of TG line.

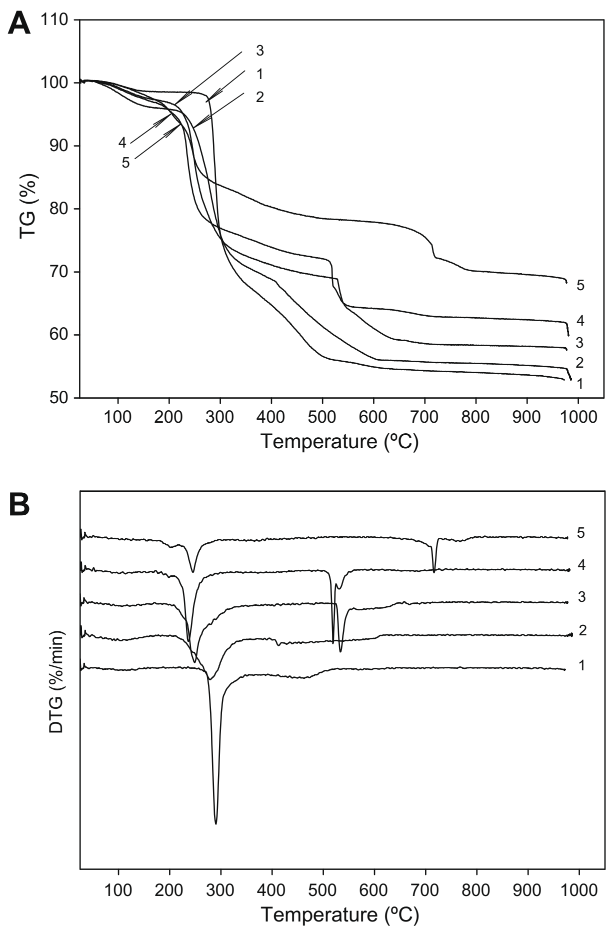


Fig. 4. TG (A) and DTG (B) curves of starch (1) and starch zincates from blends with sodium zincate at proportions starch:zincate = 1:0.05 (2), 1:0.1 (3), 1:0.25 (4), 1:0.5 (5) subjected to the 30 min microwave irradiation at 450 W.

four times shorter. However, an insight in the pattern of the TG lines (Table 2) revealed that the higher microwave power applied, accompanied with the shorter irradiation time (700 W, 1 min), provided products of somewhat different thermogravimetric characteristics. The differences were particularly noticeable in the range of 25–176 °C. The weight losses recorded within that range suggested that sodium tetrahydroxozincate and the D-glucose unit of starch, $(OH)_2$-Glc-OH, could react intramolecularly into compounds **1**, 2 or **3** (Scheme 1). Crosslinking could be involved in reaction of zincate with the D-glucose units in an intermolecular manner to form compounds **4**–**7**. Upon heating, one water molecule could be lost within the range of 25–176 °C during the decomposition of all these compounds. That decomposition fitted calculated weight losses reported in Table 3. As it could be seen, in the case of the products synthesized by microwave irradiation for 1 min with 700 W, the determined weight losses fitted very well the values calculated for compounds **1**–**3**. The compounds **4**–**7** could result from the reaction carried out on 30 min microwave irradiation with 450 W as well as on the convectional heating.

Fig. 5 shows the FT-IR spectra of zinc oxide and sodium tetrahydroxozincate. The former revealed only a strong absorption band at 470 cm^{-1} characteristic of metal–oxygen (Zn–O) stretching vibrations (Ghule, Ghule, Chen, & Ling, 2006; Singh & Gopal, 2008). The latter exhibited a broad band (3600–3000 cm^{-1}) with the maximum around 3463 cm^{-1} assigned to stretching vibrations of the hydroxyl groups probably coordinated to the Zn atoms in the salt (Sumin de Portilla, 1976). The lower frequency of that band (3250 cm^{-1}) might indicate involvement of the OH groups in hydrogen bonding. Hartert and Glemser (1953) found that there was abnormal polarization of OH groups in zinc hydroxide, and the hydrogen atom of the OH groups produced a resonance between two oxygen atoms of the hydroxyl groups. Therefore, the heating of sodium tetrahydroxozincate could lower the distance of the two OH groups and sodium oxodihydroxozincate could be formed, as determined by thermal analyses. There were also in the spectrum of sodium tetrahydroxozincate a weak band at 1654 cm^{-1}, the strong band at around 1450 cm^{-1}, as well as peaks at 880, 695, and 439 cm^{-1}. The bands at 1654 cm^{-1} and 1450 cm^{-1} could be assigned to the bending and the harmonic stretching vibrations of the OH groups, respectively (Singh & Gopal, 2008), the peaks at 880 and 695 cm^{-1} reflected the OH group vibrations in the Zn–OH entities (Sumin de Portilla, 1976), and the weak band at 439 cm^{-1} could be assigned to the Zn–O stretching vibrations of $Zn(OH)_4^{2-}$ (Briggs, Hampson, & Marshall, 1974; Fordyce & Baum, 1965).

Fig. 6 compares the FT-IR spectrum of potato starch with the spectra of samples from the processing of the 1:0.5 blends under different conditions. The spectra of all zincatated starches show the same characteristic peaks as the spectrum of starch (Table 4). However, the broad band centered at 3440 cm^{-1} turned more narrow indicating a certain ceasing of hydrogen bonds in zincatated starch in which the hydroxyl groups of D-glucose units were involved. In such manner subsequent hydroxyl groups became capable to zincatation. There was also a peak at 995 cm^{-1} which decreased and moved towards a higher wave number. That shift of the peak could result from interactions between the hydroxyl groups of D-glucose units and $Zn(OH)_4^{2-}$ moieties, and its lower intensity and deformation, to a certain extent, might correspond to the change of the crystallinity of starch upon zincatation (Sevenou, Hill, Farhat, & Mitchell, 2002). Moreover, there were additional bands in the spectrum at around 1450 and 880 cm^{-1} that could arise from the stretching vibrations of the OH groups in the Zn–OH entities. Comparing the effect of the applied power and the irradiation time, one could see that starch zincatated for longer time at lower power had sharper peaks at 1450, 995 and 880 cm^{-1} than that irradiated for a shorter time at higher power. It would suggest that in the former case the treatment applied offered better conditions for zincatation than in the latter case, where the higher power damaged the starch macrostructure to a higher extent. No clear differences between the spectra of starch zincatated by convectional heating and microwave irradiation (450 W, 30 min) were observed.

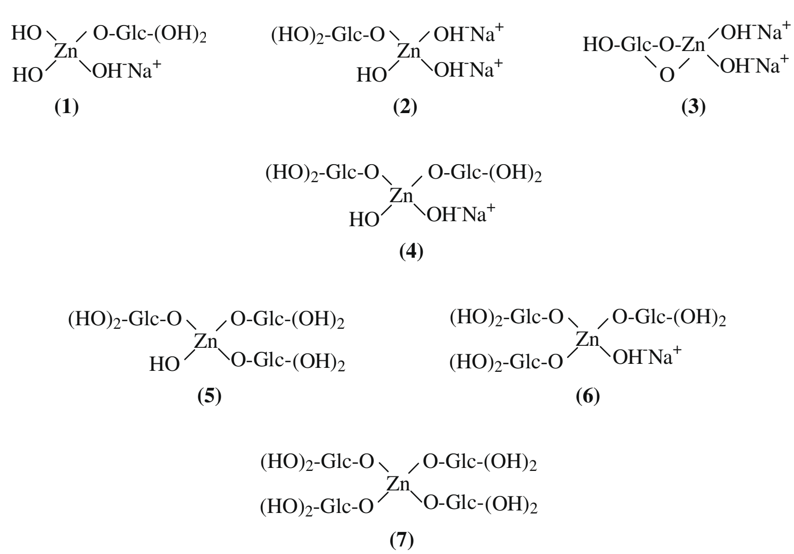
Differential FT-IR spectra of zincatated starch presented in Fig. 7 provided an evidence that starch and $Na_2Zn(OH)_4$ formed a derivative in which the hydroxyl groups of the D-glucose units and Zn–OH of $Na_2Zn(OH)_4$ were involved. The spectrum of zincatated starch from which the spectrum of starch was subtracted (the differential spectrum in Fig. 7A) revealed a negative absorption band at about 3250 cm^{-1} and positive peaks at 1450 and 880 cm^{-1}. In the spectrum of zincatated starch from which the spectrum of $Na_2Zn(OH)_4$ was subtracted (the differential spectrum in Fig. 7B), all positive peaks characteristic of the starch spectrum were observed, except negative peaks at about 1480, 1430 and 880 cm^{-1}.

As found in earlier studies (Bączkowicz, Wójtowicz, Anderegg, Schilling, & Tomasik, 2003; Mao et al., 2006; Staroszczyk, 2009a, 2009b; Staroszczyk et al., 2007), the reaction of starch with two- and multi-functional reagents could proceed with the formation of intermolecular bonds between individual chains of starch polysaccharides, i.e. with crosslinking. The TG/DTG and FT-IR analysis unambiguously indicated the $Na_2Zn(OH)_4$ formation rather than Na_2ZnO_2, in which the zinc ion was tetrahedrally coordinated. That explains why starch could react with this complex compound to form both monoesters, compounds **1–3**, and crosslinked esters,

Table 2
Thermogravimetric characteristics of starch zincatation products.

Sample	Temperature range (°C)	Microwave heating						Convectional heating		
		30 min at 450 W			1 min at 700 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										
	25–176	1.63			6.20		112	2.83		
	176–491	41.40	1.40	291	37.95	1.35	288	41.08	1.71	290
	491–650	6.00			6.65			6.67		
	650–970	1.15			0.40			0.68		
	Total	50.18			51.20			51.26		
Starch:zincate										
1:0.05	25–176	4.01			6.04		105	2.53		
	176–491	34.12	0.41	279	31.85	0.43	278	33.68	0.35	278
	491–650	6.01			6.29			6.67		
	650–970	1.15			0.41			0.69		
	Total	45.29			44.59			43.57		
1:0.1	25–176	2.73			5.90		111	2.42		
	176–491	27.91	0.58	249	25.90	0.35	257	28.82	0.88	247
	491–650	10.20		533	8.83		528	9.92		525
	650–970	1.22			1.85		697	1.30		
	Total	42.02			42.46			42.45		
1:0.25	25–176	3.26			5.14		102	2.99		
	176–491	24.52	0.56	237	21.73	0.60	236	24.66	0.63	234
	491–650	8.43		517, 532sh	8.21		516, 526sh	8.10		515, 528sh
	650–970	1.81			1.80			2.57		
	Total	37.98			36.94			38.39		
1:0.5	25–176	2.83			5.08		128	3.01		
	176–491	18.61	0.30	202sh, 246	16.78	0.20	202sh, 250	19.43	0.36	203sh, 247
	491–650	1.27			1.03			1.28		
	650–970	8.35		710	7.27		714	8.30		708
	Total	31.07			30.19			32.07		

[a] The weight loss [%] within the specified temperature range.
[b] The slope of TG line.



Scheme 1. Possible structures of zincatated starch.

compounds **4–7** (Scheme 1). The results found for the reaction products proved that the prolonged reaction time favoured crosslinking of starch. The microwave irradiation for 1 min at 700 W resulted in the monoesters formation, while the 30 min microwave irradiation at 450 W and convectional heating for 120 min at 100 °C led to intermolecular crosslinking. It should be emphasized, however, that in both cases sodium hydroxide simultaneously formed. On one hand, by penetrating freely into the structure of starch granules, it could cause swelling of granules in their amorphous domains whereby they partially lost crystalline properties. On the other hand, an increase in the volume due to swelling, facilitated the zincatation.

The differences observed in the diffraction patterns of the native potato starch and the samples from the processing of the 1:0.05 and 1:0.5 blends indicated the loss of crystalline structure of potato starch as the zincatation progressed (Fig. 8). One could see that while the samples irradiated without as well as with the lowest dose of zincate still exhibited partial crystallinity represented by

Table 3
Calculated and found weight losses associated with the decomposition of starch zincates in the range of 25–176 °C.

Compound[a]	Monoesters			Crosslinked esters			
	1	2	3	4	5	6	7
Weight loss (%)							
Calculated[b]	5.99	5.57	5.89	4.05	3.18	3.06	2.54
Found[c]	Starch:zincate = 1:0.05						
Microwave irradiated							
450 W, 30 min				4.01			
700 W, 1 min	6.04						
Convectionally heated							
100 °C, 120 min							2.53
	Starch:zincate = 1:0.1						
Microwave irradiated							
450 W, 30 min							2.73
700 W, 1 min			5.90				
Convectionally heated							
100 °C, 120 min							2.42
	Starch:zincate = 1:0.25						
Microwave irradiated							
450 W, 30 min					3.26		
700 W, 1 min		5.14					
Convectionally heated							
100 °C, 120 min						2.99	
	Starch:zincate = 1:0.5						
Microwave irradiated							
450 W, 30 min						2.83	
700 W, 1 min		5.08					
Convectionally heated							
100 °C, 120 min						3.01	

[a] The notation of compounds according to Scheme 1 and the text.
[b] The calculations for the elimination of one molecule of water.
[c] Found from the thermograms.

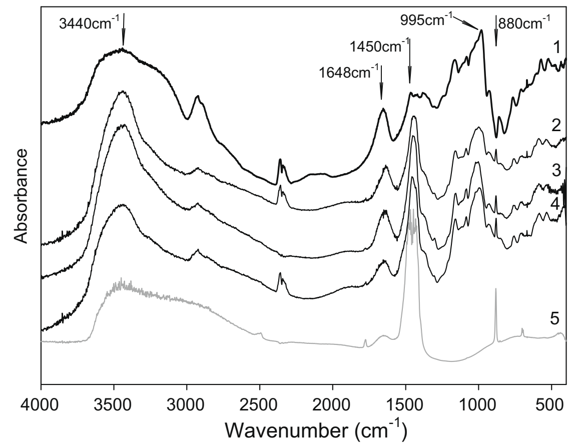


Fig. 6. FT-IR spectra of potato starch (1), and samples from the processing of the 1:0.5 blends in different conditions: microwave irradiation with 700 W for 1 min (2), 450 W for 30 min (3), convectional heating at 100 °C for 120 min (4). Spectrum of $Na_2Zn(OH)_4$ (5) is shown for comparison.

Table 4
Band assignments in the FT-IR spectra of native potato starch.

Band position (cm^{-1}) and intensity[a]	Band assignment
3440 s	ν_{OH} intramolecular hydrogen bond
2928 m	ν_{CH}
1648 w	$\nu_{C=O}$, δ_{OH} polymer bound water
1432 m	δ_{OH}, δ_{CH}
1377 m	δ_{OH}, δ_{CH}
1162 s	δ_{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

[a] vs – very strong; s – strong; m – medium; w – weak; vw – very weak.

peaks at 17° and 22.2° 2θ, the sample with the highest dose of the agent lost crystallinity completely.

The changes in melting temperature and the melting enthalpy confirmed the significant loss of crystallinity of the starch caused by the zincatation process (Table 5). Only the values for the samples with the lowest doses of the zincating agent could be determined. The samples prepared by the microwave-assisted (450 W, 30 min) and convectional heating methods displayed similar thermal properties, which was reflected by the comparable calorimetric parameters.

Zincate concentration-dependent changes in aqueous solubility (AS) and water binding capacity (WBC) pointed out that the integrity of the starch granules was weakened and swelling was facilitated. Both AS and WBC increased with an increase in the zincate concentration (Table 6). Insight in Table 6 revealed that the microwave irradiation for 30 min at 450 W and convectional heating for 120 min at 100 °C resulted mostly in the products of WBC higher, and AS lower, than the products formed under microwave irradiation for 1 min at 700 W. Such features would indicate formation of crosslinked product in the former case. An increased solubility of the crosslinked material, much higher than that of native, non-crosslinked starch, could result from an alkaline degradation of starch after its zincatation. On the other hand, either prolonged irradiation or heating time cancelled hydrogen bonds in which the hydroxyl groups of D-glucose units participated. Their presence in zincatated starch also increased the AS and WBC.

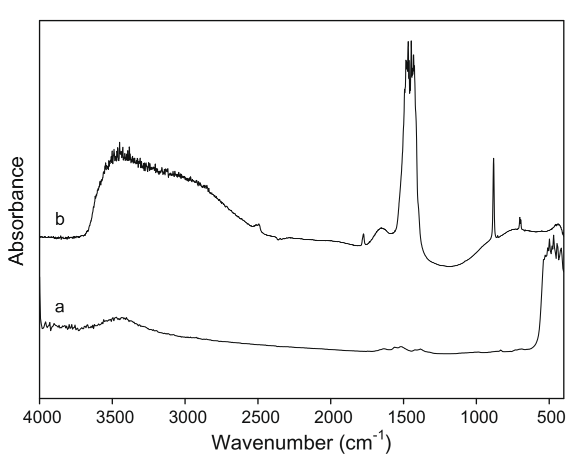


Fig. 5. FT-IR spectra of zinc oxide (a) and sodium tetrahydroxozincate (b).

4. Conclusions

The most important results obtained in the presented research can be summarized as follows:

1. Zincatation of starch using microwave irradiation in a solid-state reaction is a facile method of synthesis of zinc derivatives of starch.
2. $Na_2Zn(OH)_4$ rather than Na_2ZnO_2 was the reagent in which $Zn(OH)_4^{2-}$ moieties were multi-functional groups responsible for polymer network formation in starch.
3. Depending on the irradiation conditions, the microwave-assisted zincatation led to the products of either mono- or crosslinking esterification.

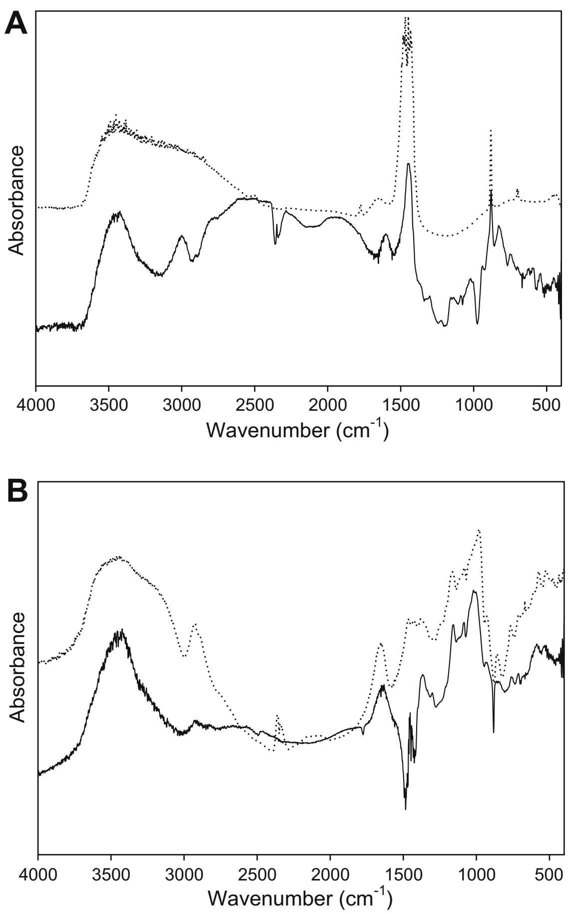


Fig. 7. Differential FT-IR spectra of the sample prepared on the microwave irradiation (450 W, 30 min) of the 1:0.5 blend, from which the spectra of starch (A) and $Na_2Zn(OH)_4$ (B) were subtracted (solid lines). The spectra of $Na_2Zn(OH)_4$ (A) and starch (B) are shown for comparison (dotted lines).

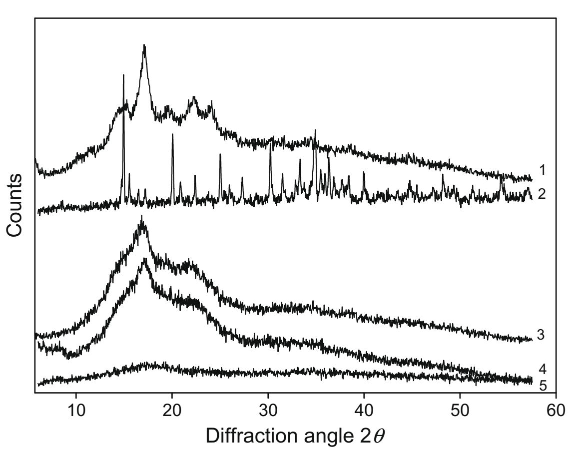


Fig. 8. Powder X-ray diffractograms of native potato starch (1), sodium tetrahydroxozincate (2), starch after microwave irradiation with 450 W for 30 min (3) and samples form the processing of the 1:0.05 (4) and 1:0.5 (5) blends at the same microwave irradiation condition.

4. Higher power applied at shorter exposition offered products of monoesterification, but was simultaneously more damaging to the starch macrostructure, and lower power at longer exposition favoured crosslinking of starch.
5. The microwave irradiation provides essentially reduced reaction time required for complete zincatation.

Table 5
DSC calorimetric parameters for potato starch and its zincates.[a]

Sample	T_o (°C)[b]	T_p (°C)[b]	T_c (°C)[b]	ΔT (°C)[b]	ΔH (J/g)[b]
Potato starch					
Native	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
700 W, 1 min	64.9	67.8	71.5	6.6	15.4
		Starch:zincate = 1:0.05			
Convectionally heated					
100 °C, 120 min	43.1	48.6	58.5	15.4	5.9
Microwave irradiation					
450 W, 30 min	44.6	50.9	56.8	12.2	6.0
700 W, 1 min	56.8	61.1	66.1	9.3	9.5
		Starch:zincate = 1:0.1			
Convectionally heated					
100 °C, 120 min	n.o[c]	n.o.	n.o.	n.o.	n.o.
Microwave irradiation					
450 W, 30 min	n.o.	n.o.	n.o.	n.o.	n.o.
700 W, 1 min	51.6	57.7	62.5	10.9	8.6

[a] The standard deviation of all estimations did not exceed ±10% of determined value.
[b] Onset (T_o), peak (T_p) and conclusion (T_c) melting temperatures, melting temperature interval (ΔT) and melting enthalpy (ΔH).
[c] Not observed. For the potato starch:sodium zincate ratio of 1:0.25 and 1:0.5 no values could be determined.

Table 6
Water binding capacity (WBC) and aqueous solubility (AS) of the starch zincates.[a]

Sample	Microwave heating		Convectional heating
	30 min at 450 W	1 min at 700 W	120 min at 100 °C
Water binding capacity (g/g)[b]			
Potato starch	14.66 ± 1.42	13.65 ± 1.33	9.06 ± 4.52
1:0.05	8.12 ± 1.52	10.21 ± 1.07	8.78 ± 2.06
1:0.1	15.74 ± 0.97	11.22 ± 0.10	15.84 ± 1.75
1:0.25	36.02 ± 0.85	19.03 ± 1.88	34.47 ± 3.39
1:0.5	24.62 ± 1.33	27.13 ± 2.13	51.07 ± 1.55
Aqueous solubility (%)[b]			
Potato starch	6.56 ± 0.30	0.57 ± 0.03	0.06 ± 0.03
1:0.05	4.62 ± 0.47	5.87 ± 0.40	4.54 ± 0.35
1:0.1	8.83 ± 0.21	10.86 ± 0.40	8.98 ± 0.23
1:0.25	20.36 ± 0.31	20.59 ± 0.81	18.64 ± 0.42
1:0.5	45.27 ± 4.43	42.64 ± 4.20	30.08 ± 2.72

[a] Means of four measurements ± standard deviation.
[b] The WBC of the native potato starch was 11.72 (g/g) ± 0.23 and AS 0.41 (%) ± 0.14.

6. The structure of zincatated starch depends on the zincate concentration.

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References

Bączkowicz, M., Wójtowicz, D., Anderegg, J. W., Schilling, C. H., & Tomasik, P. (2003). Starch complexes with bismuth (III) and (V). *Carbohydrate Polymers, 52*, 263–268.

Bandwar, R. P., Giralt, M., Hidalgo, J., & Rao, C. P. (1996). Metal-saccharide chemistry and biology: Saccharide complexes of zinc and their effect on metallothionein synthesis in mice. *Carbohydrate Research, 284*, 73–84.

Briggs, A. G., Hampson, N. A., & Marshall, A. (1974). Concentrated potassium zincate solutions studied using laser Raman spectroscopy and potentiometry. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics, 70*, 1978–1990.

Dirkse, T. P., Postmus, C., Jr., & Vandenbosch, R. (1954). A study of alkaline solutions of zinc oxide. *Journal of the American Chemical Society, 76*(23), 6022–6024.

Fordyce, G. S., & Baum, R. L. (1965). Vibrational spectra of solutions of zinc oxide in potassium hydroxide. *The Journal of Chemical Physics, 43*, 843–846.

Gerard, C., Colonna, P., Buleon, A., & Planchot, V. (2001). Amylolysis of maize mutant starches. *Journal of the Science of Food and Agriculture, 81*, 1281–1287.

Ghule, K., Ghule, A. V., Chen, B.-J., & Ling, Y.-Ch. (2006). Preparation and characterization of ZnO nanoparticles coated paper and its antibacterial activity study. *Green Chemistry, 8*, 1034–1041.

Hartert, E., & Glemser, O. (1953). Zur Lage des Wasserstoffs im Gitter kristalliner Hydroxyde. *Naturwissenschaften, 40*, 199–200.

Jyothi, A. N., Rajasekharan, K. N., Moorthy, S. N., & Sreekumar, J. (2005). Microwave-assisted synthesis and characterization of succinate derivatives of cassava (*Manihot esculenta* Crantz) starch. *Starch/Stärke, 57*, 556–563.

Lacroix, M. (2009). Mechanical and permeability properties of edible films and coatings for food and pharmaceutical applications. In M. E. Embuscado & K. C. Huber (Eds.), *Edible films and coatings for food applications* (pp. 347–366). New York: Springer.

Lewandowicz, G., Fornal, J., Walkowski, A., Mączyński, M., Urbaniak, G., & Szymańska, G. (2000). Starch esters obtained by microwave radiation – Structure and functionality. *Industrial Crops and Products, 11*, 249–257.

Mao, G.-J., Wang, P., Meng, X.-S., Zhang, X., & Zheng, T. (2006). Crosslinking of corn starch with sodium trimetaphosphate in solid state by microwave irradiation. *Journal of Applied Polymer Science, 102*, 5854–5860.

Pandaya, K. I., Russel, A. E., McBreen, J., & O'Grady, W. E. (1995). EXAFS investigations of Zn(II) in concentrated aqueous hydroxide solutions. *The Journal of Physical Chemistry, 99*, 11967–11973.

Richter, M., Augustat, S., & Schierbaum, F. (1968). *Ausgewählte Methoden der Stärkechemie*. Leipzig: VEB Fachbuch Verlag.

Rutiaga, M. O., Galan, L. J., Morales, L. H., Gordon, S. H., Imam, S. H., Ortes, W. J., et al. (2005). Mechanical property and biodegradabilility of cast films prepared from blends of oppositely charged biopolymers. *Journal of Polymers and the Environment, 13*(2), 185–191.

Sevenou, O., Hill, S. E., Farhat, I. A., & Mitchell, J. R. (2002). Organization of the external region of the starch granule as determined by infrared microscopy. *International Journal of Biological Macromolecules, 31*, 79–85.

Shogren, R. L., & Biswas, A. (2006). Preparation of water-soluble and water-swellable starch acetates using microwave heating. *Carbohydrate Polymers, 64*, 16–21.

Singh, S. C., & Gopal, R. (2008). Laser irradiance and wavelength-dependent compositional evolution of inorganic ZnO and ZnOOH/organic SDS nanocomposite material. *The Journal of Physical Chemistry C, 112*, 2812–2819.

Smith, G. D., Bell, R., Borodin, O., & Jaffe, R. L. (2001). A density functional theory study of the structure and energetics of zincate complexes. *The Journal of Physical Chemistry A, 105*, 6506–6512.

Stahl, R., Niewa, R., & Jacobs, H. (1999). Synthese und kristallstructur von $Na_2Zn(OH)_4$. *Zeitschrift für anorganische und allgemeine Chemie, 625*, 48–50.

Staroszczyk, H. (2009a). Microwave-assisted boration of potato starch. *Polimery, 54*, 31–41.

Staroszczyk, H. (2009b). Microwave-assisted silication of potato starch. *Carbohydrate Polymers, 77*, 506–515.

Staroszczyk, H., Fiedorowicz, M., Zhong, Wei., Janas, P., & Tomasik, P. (2007). Microwave-assisted solid-state sulphation of starch. *e-Polymers* [No. 140].

Staroszczyk, H., & Tomasik, P. (2005). Facile synthesis of potato starch sulfate magnesium salts. *e-Polymers* [no. 080].

Staroszczyk, H., Tomasik, P., Janas, P., & Poreda, A. (2007). Esterification of starch with sodium selenite and selenate. *Carbohydrate Polymers, 69*, 299–304.

Sumin de Portilla, V. I. (1976). The nature of hydrogen bonds and water in legrandite by IR spectroscopy. *American Mineralogist, 61*, 95–99.

Tomasik, P., & Schilling, Ch. H. (2004). Chemical modification of starch. *Advances in Carbohydrate Chemistry and Biochemistry, 59*, 175–403.

Woo, K., Bassi, S. D., Maningat, C. C., Ganjyal, G. M., & Zhao, L. (2006). Mineral-bound starch compositions and methods of making same. US Patent Application, Pat. No. 0286285 (A1).

Xing, G. X., Zhang, S. F., Ju, B. Z., & Yang, J. Z. (2006). Microwave-assisted synthesis of starch maleate by dry method. *Starch/Stärke, 58*, 464–467.