

Synthesis and characterisation of starch cuprate

Hanna Staroszczyk *

Department of Food Chemistry, Technology and Biotechnology, Chemical Faculty, Gdansk University of Technology, Narutowicza Street 11/12, 80-233 Gdansk, Poland

a b s t r a c t

The cupration of granular potato starch with ammonium tetrachlorocuprate(II) was performed by a 20 min lasting microwave-assisted process and by 40 min convectional heating. In both cases the degree of esterification (DE) did not exceed 6.4×10^{-3} . A higher dose of cuprate had a positive effect on DE, regardless of whether the microwave irradiation or the convectional heating was applied, and on the thermal stability of the starch cuprate produced in the microwave-assisted way. As a result of cupration, the hydroxyl ligand of the starch D-glucose units was replaced by the chloride ligand of the tetrachlorocuprate(II) anion. In the starch cuprate formed in the microwave-assisted process, the cuprate anion additionally coordinated water molecules. The cupration reduced starch crystallinity, as indicated by X-ray diffractometry and differential scanning calorimetry.

Keywords: Microwave-assisted reactions, Potato starch, Cupration

1. Introduction

The hydroxyl groups of starch polysaccharides (amylose and amylopectin) react in a way typical of primary and secondary alcohols, that is, among others, they form metal derivatives resembling alcoholates and esters. Such reactions leading to Al, Bi(III), Fe(III), La, Na, Sb(V), Sn(IV), Ti(IV), Tl(I), and Zr(IV) derivatives have been reviewed by Tomasik and Schilling (2004). This project on starch cupration with ammonium tetrachlorocuprate(II) has been induced by a recently published (Staroszczyk & Janas, 2010a) successful zincation of starch. Presented results extend a list of known starch metal derivatives.

Copper is one of essential bioelements. In association with proteins or enzymes, it is an integral part of the catalytic centers at which the biochemical reactions in human cells proceed. Copper is involved in the formation of haemoglobin and red blood cells. It is also required for free radical detoxification, collagen synthesis, and bone development. Copper(II) tetrahalides are often used as model compounds for the active sites in, for example, metalloenzymes or metalloproteins (Penfield, Gewirth, & Solomon, 1985).

Starch, in contrast to simple sugars, has been shown to have no influence on the advance of copper deficiency anaemia in living organisms, while the replacement of simple sugars with starch in the diet of anaemic copper-deficient organisms increases the haemoglobin levels (Johnson & Gratzek, 1986). Complexing of starch with copper minerals can give an opportunity to include this bioelement in starch-containing food, cosmetics and pharmaceutical compositions, and in this way, to influence copper-requiring

chemical and biochemical reactions in living organisms. Copper ions adsorbed by different modified starches (Śmigielska & Lewandowicz, 2007), as well as bound to phosphorylated cross-linked starch (Woo, Bassi, Maningat, Ganjyal, & Zhao, 2006), exhibit remarkable functional and nutritional properties. Complexes of copper with starch were reported to have disinfecting properties (Stern, 1926) and were patented as useful materials for accelerating wound healing and increasing the rate of hair growth (Pickart, 1999).

The interaction of starch with compounds containing bioelements, resulting in starch complexes formation, has been extensively studied. The results of these studies demonstrate that salts containing metal ions from transition groups, among them also Cu(II) ions, form Werner-type complexes. In these complexes, the central metal atom is ligated through the oxygen atoms of the hydroxyls of D-glucose units (D-Glc) (Ciesielski, Lii, Yen, & Tomasik, 2003; Ciesielski & Tomasik, 2003a, 2003b, 2004a, 2004b).

Potato starch, unlike other starches, is naturally esterified with phosphoric acid in its D-Glc of amylopectin fraction. Therefore, this starch contains metal cations bound to the phosphate group which make it capable of binding a number of metal ions to phosphate moieties utilising the cation-exchanging properties (Leszczyński, 1985). When the metal ion comes from a transition group, it is additionally ligated by starch because of outer electronic shell with vacancy resulting from binding to phosphate groups (Ciesielski & Tomasik, 2004a, 2004b; Śmigielska, Lewandowicz, Goslar, & Hoffmann, 2005).

In starch transition metal alkoxides (Tomasik, Anderegg, Baczkowicz, & Jane, 2001; Tomasik, Schilling, Anderegg, & Refvik, 2000; Tyrlik, Tomasik, Anderegg, & Baczkowicz, 1997) the metal atoms are bound to starch via an oxygen atom of the 6-hydroxyl group of the D-Glc, with co-coordination to other oxygen atoms

present in these units. Additionally, the involvement of two alkoxide groups in the reaction causes cross-linking of starch.

Esterification of starches produces anionic starches. Esterification takes place preferentially with the involvement of the 6-hydroxyl and 3-hydroxyl groups of the D-Glc (Bindzus, Altieri, Kasica, & Trzasko, 2002). Since the lone pairs of electrons of the oxygen atom of the hydroxyl groups make starch nucleophile, the effect of esterification with mineral acids and/or salts depends, first of all, on the electron gap at the central atom of these compounds (Staroszczyk, 2009a, 2009b; Staroszczyk, Tomasik, Janas, & Poreda, 2007). Moreover, as demonstrated in the microwave-assisted processes, if the esterifying agent is multibasic, besides monoesters (Lewandowicz, Szymańska, Voelkel, & Walkowski, 2000), also cross-linked esters can be formed, with the involvement of at least two reaction centers of the esterifying agent (Fortuna, 1998; Mao, Wang, Meng, Zhang, & Zheng, 2006; Staroszczyk, 2009a, 2009b; Staroszczyk, Fiedorowicz, Zhong, Janas, & Tomasik, 2007; Staroszczyk & Janas, 2010a, 2010b; Staroszczyk & Tomasik, 2005; Staroszczyk et al., 2007). Cancellation of intra- and inter-molecular hydrogen bond residing in native starch by covalent bonds in cross-linked starch, as well as possible hydrogen bonding between the hydroxyl groups of the D-Glc and introduced acid moieties, certainly contribute to the functional properties of starch.

The objective of this study was to examine the esterification of potato starch with ammonium tetrachlorocuprate(II) in the solid state process. Starch cuprate, as a material of anionic character, could find application as a potential component of pharmaceutical compositions which can readily combine with materials of cationic character, for instance, with proteins. To determine optimal conditions for the preparation of esters, the microwave irradiation and, for comparison, the convectional heating was applied.

2. Materials and methods

2.1. Preparation method

Native potato starch (13% moisture), isolated in Potato Enterprise in Łomża (Poland), and >99% ammonium tetrachlorocuprate(II) dihydrate (Fluka, 00634), were blended at proportions of 1:0.1 and 1:1 (mole D-glucose unit/mole copper compound), and were then thoroughly homogenised in an agate mortar. The final blends (2 g) of 13% moisture content were irradiated in a Samsung M1711N microwave oven either at 450 W for 8 and 20 min for 1:0.1 and 1:1 blends, respectively, or at 800 W for 3 min. For comparison, the starch-cuprate blends were also convectionally heated in a LG MC-8084 NLC oven at 100 °C for 40 min. The pH value at the end of the reaction was ~6, and the final temperature in the case of the microwave irradiation at 450 W for 20 min amounted to 70 °C, and in the case of the microwave irradiation at 450 for 8 min and 800 W for 3 min, 65 °C. The reaction products were washed with ice water (30 ml) on a suction filter, dried at 40 °C for 24 h, and then stored in tightly closed vessels.

2.2. Analysis

2.2.1. Chemical composition

The nitrogen content of starch derivatives was determined according to PN-EN ISO 3188 Standard (2000). A SOLAAR S4 atomic absorption spectrophotometer, ThermoElemental (Madison, WI, USA) was used for the determination of the total copper content in the samples after their wet digestion with 1:4 mixture of concentrated sulphuric and nitric acids. All estimations were run in duplicates.

2.2.2. Determination of the degree of esterification (DE)

From the content of Cu determined by elemental analysis, the DE was calculated by comparing the experimental values with the theoretical values calculated for the applied proportions of the reagents 1:0.1 and 1:1 (starch:ATCI-Cu).

2.2.3. Thermal analysis (TG and DTG)

Thermogravimetric analysis was performed with a TG/SDTA Mettler-Toledo 851^e apparatus (Greifensee, Switzerland) 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 cm³/min), within temperature range of 25–600 °C, at a heating rate of 10 °C/min.

2.2.4. 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 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹, using a Matson 3000 FT-IR (Madison, WI, USA) spectrophotometer.

2.2.5. Differential scanning calorimetry (DSC)

The samples (~8 mg) were sealed in aluminium pans with water at the 1:3 weight ratio, left for 1 h for equilibration, and subsequently scanned at the rate of 6 °C/min in the temperature range of 20–90 °C. A Mettler TA3000 calorimeter (Greifensee, Switzerland), equipped with a TC 10 TA processor and a DSC 30 temperature cell, was used with an empty pan as a reference. The instrument was calibrated against pure indium ($T_m = 156.6$ °C and $\Delta H_m = 28.45$ J/g). Analyses were run in triplicates.

2.2.6. Powder X-ray diffractometry

The crystalline structure of the samples was determined according to Gerard, Colonna, Buleon, and Planchot (2001). The measurements were carried out by applying CuK 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° 2 θ were recorded at a scan rate of 0.02° 2 θ /s.

2.2.7. Aqueous solubility and water binding capacity

The aqueous solubility (AS) and water binding capacity (WBC) at room temperature were estimated according to Richter, Augustat, and Schierbaum (1968). Estimations were run in 10 repetitions.

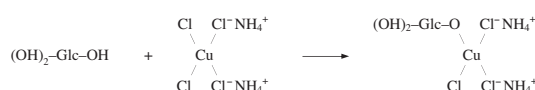
2.2.8. Statistical analysis

The data obtained from the DSC thermal analysis and from the AS and WBC analysis were statistically analysed by one-way analysis of variance to determine significant differences among samples, using STATGRAPHICS version 2.1 (Statistical Graphics Corporation, USA). Significance was accepted at $p < 0.05$.

3. Results and discussion

3.1. Progress of the reaction

Derivatisation of starch was carried out on either microwave irradiation or convectional heating of potato starch with varying the amount of ammonium tetrachlorocuprate(II) dihydrate (ATCI-Cu) complex. The resulting starch cuprate (Scheme 1) had a degree of esterification (DE) $\leq 6.4 \times 10^{-3}$, regardless of the mode of



Scheme 1. Cupration of potato starch with ATCI-Cu.



Table 1
Chemical characteristics of potato starch cupration products.^a

Sample starch:ATCl-Cu	wt.%											
	Calculated ^b		Found									
			Microwave irradiation						Convectional heating			
			450 W		DE ^c × 10 ⁻³		800 W		DE ^c × 10 ⁻³		100 °C	DE ^c × 10 ⁻³
	Cu	N	Cu	N			Cu	N		Cu	N	
1:0.1	3.48	1.54	0.07 ± 0.005	0.03 ± 0.003	2.1		0.13 ± 0.01	0.06 ± 0.005	3.7	0.09 ± 0.009	0.04 ± 0.004	2.6
1:1	17.32	7.64	0.11 ± 0.01	0.05 ± 0.004	6.4		0.10 ± 0.01	0.04 ± 0.003	5.8	0.11 ± 0.01	0.05 ± 0.005	6.4

^a Means of two measurements ± standard deviation.

^b Assuming 100% reaction yield.

^c Degree of esterification was calculated on the basis of the content of Cu determined by elemental analysis, by comparing experimental values with theoretical values calculated for the applied proportions of the reagents 1:0.1 and 1:1 (starch:ATCl-Cu).

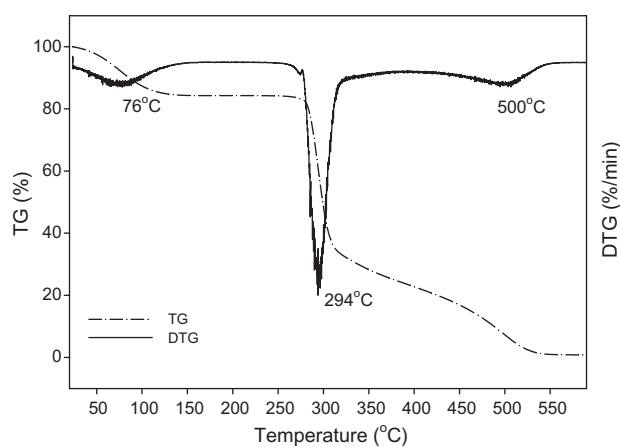


Fig. 1. Thermogram of native potato starch.

esterification (Table 1). DE slightly rose with an increase in the dose of ATCl-Cu. The microwave-assisted reaction offered a significant reduction in the reaction time but an increase in the power applied had no positive effect upon DE. A lower power applied (450 W) provided a 3-fold increase in DE, whereas a higher power (800 W) gave only a 1.5-fold increase in DE with an increasing dose of ATCl-Cu. That effect could be associated with a temperature dependent change of the ATCl-Cu coordination geometry (Fukuda, 2007). At low temperatures, the N–H–Cl hydrogen bonds between ammonium cation and the tetrachlorocuprate(II) anion (CuCl_4^{2-}) reduced the electron density in the CuCl_4^{2-} and, in consequence, the negative charge at chlorine decreased and the ligand–ligand repulsion weakened. Then, the square-planar geometry stabilised in the solid. At high temperatures, the N–H–Cl hydrogen bonds between NH_4^+ and CuCl_4^{2-} broke and the ligand–ligand repulsion became stronger, which in turn resulted in a distortion of the

CuCl_4^{2-} toward a tetrahedral geometry. This ability of rearrangement of the configuration of the CuCl_4^{2-} with temperature (associated with a change of a colour in the solid) probably facilitated the esterification of starch at low temperatures (the stronger the N–H–Cl hydrogen bonds, the lower the electron density in CuCl_4^{2-}), and made the reaction difficult when the microwave irradiation or the convectional heating increased the temperature (the weaker N–H–Cl hydrogen bonds, the stronger the Cl–Cl electrostatic repulsion in CuCl_4^{2-}).

The thermogram presented in Fig. 1 shows a one-step decomposition of starch taking place within the temperature range of 260–330 °C, with a DTG peak at 294 °C and 56.3% weight loss (see also Table 2).

The sample of ATCl-Cu decomposed up to 600 °C in three steps (Fig. 2), losing 13.56%, 45.86% and 34.42% of the initial weight, respectively. The first weight loss, with a minimum on the DTG line at 154 °C, fitted fairly well an expected loss of two water molecules of crystallisation (13.00% calculated weight loss). The second step, with a minimum centered at 308 °C, corresponded to the formation of cupric chloride, however, the weight loss of 45.86% determined from the thermogram did not fit exactly the calculated value of 38.5%. Above 350 °C, in the third step, a further weight loss was observed. At the final temperature of 600 °C, the reduction of cupric chloride to cuprous chloride was possible, with a metallic copper formation in the final stage of the decomposition (Judd, Plunkett, & Pope, 1975). However, the weight loss of 34.42% from the thermogram compared rather poorly with the calculated value of 25.6%.

The thermal decomposition of ATCl-Cu might be represented as:

Step 1

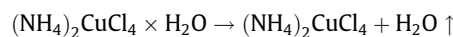
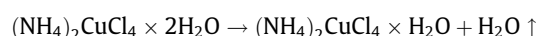


Table 2
Thermogravimetric characteristics of native potato starch and ATCl-Cu.

Sample	Temperature range (°C)	Weight loss (%) ^a	Slope (tg α) ^b	DTG peak temperature (°C)
Native starch	25–165	15.72	2.86	76
	165–352	56.29		294
	352–600	27.20		500
	Total	99.21		
ATCl-Cu	25–165	13.56		136, 153
	165–352	45.86		308
	352–600	34.42		550
	Total	93.84		

^a Weight loss (%) in the specified temperature ranges.

^b The slope of TG line.

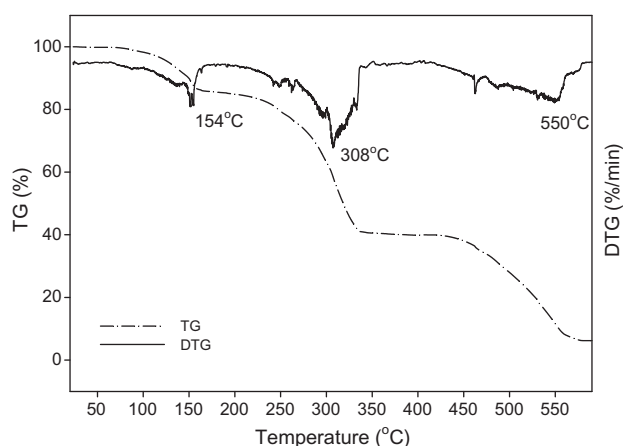


Fig. 2. Thermogram of ATCl-Cu.

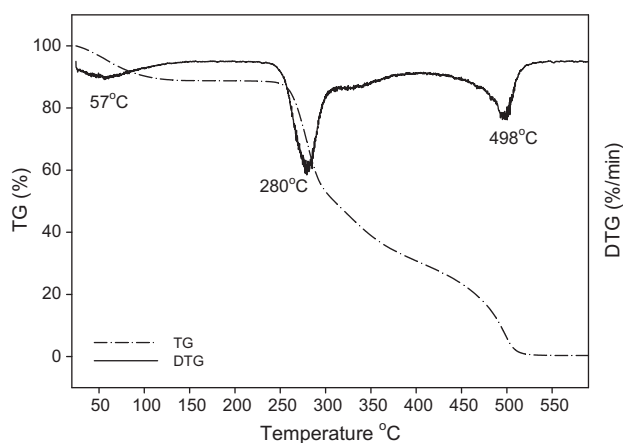
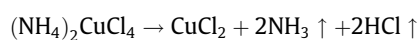


Fig. 3. Thermogram of the product from microwave irradiation with 800 W of 1:1 potato starch:ATCl-Cu blends.

Step 2



Step 3



Table 3
Thermogravimetric characteristics of potato starch cupration products.

Sample	Temperature range (°C)	Microwave irradiated						Conventionally heated		
		450 W			800 W			100 °C		
		Weight loss (%) ^a	Slope (tg α) ^b	DTG ^c (°C)	Weight loss (%)	Slope (tg α)	DTG (°C)	Weight loss (%)	Slope (tg α)	DTG (°C)
Starch	25–165	2.74	3.06	95	6.45	2.86	73	10.46	3.03	85
	165–352	64.82		294	61.31		292	59.13		294
	352–600	31.86		500	32.03		496	29.69		500
1:0.1 ^d	25–165	10.62 (3.72) ^e	0.97	68	10.23 (7.09)	1.02	71	8.72 (10.74)	1.30	75
	165–352	47.04		277	48.75		277	51.62		282
	352–600	42.24		519	40.69		506	39.31		507
1:1	25–165	9.93 (8.15)	1.26	75	11.22 (10.01)	1.30	57	10.69 (12.01)	1.30	60
	165–352	51.48		279	50.26		280	50.83		279
	352–600	38.45		484	38.17		498	38.29		509

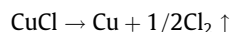
^a Weight loss (%) in the specified temperature ranges.

^b The slope of TG line.

^c DTG peak temperature.

^d Starch:ATCl-Cu (mole D-glucose unit/mole ATClCu) initial ratio.

^e Weight loss calculated based on the thermograms of particular components of the product is given in parentheses.



Since the total weight loss read from the thermogram disagrees with the value calculated for the reactions shown in the above formulas (93.84% against 77.1%), this indicated that the original ATCl-Cu contained some impurities. Moreover, since the thermogravimetric analysis was conducted in the air, oxidation might have occurred.

Fig. 3 depicts an example thermogram of starch cuprate. The thermograms of all samples of starch cuprate differed only slightly from one another. The slopes of the TG line revealed their more complex decomposition than that of native starch, and the DTG peak appearing within the temperature range of 260–330 °C pointed to their lower thermal stability; the temperature was several degrees lower than the decomposition of starch, irrespective whether the microwave irradiation or the convectional heating was applied to obtain them (Table 3). Contrary to the products from convectional heating, the thermal stability of starch cuprate from the microwave-assisted reaction increased when a higher dose of ATCl-Cu was used. However, an increase in the power applied had no effect upon these features. The insignificant increase in the thermal stability could support the hydrogen bond interactions between introduced cuprate anion and the hydroxyl groups of D-Glc rather than the formation of cross-linked products. The formation of these hydrogen bonds seemed to be an essential factor for the progress of the reaction, because it replaced the N–H–Cl hydrogen bonds between NH_4^+ and CuCl_4^{2-} in the reaction conditions.

An insight in the pattern of the TG lines also revealed that the products from microwave irradiation, unlike those from convectional heating, held the water, as their actual weight loss in the range 25–165 °C exceeded that calculated from the thermograms of the particular components of the products.

The FT-IR spectrum of ATCl-Cu is shown in Fig. 4. The broad absorption band centered at 3160 cm^{-1} represented the N–H stretching vibrations in ammonium salt, the band of strong intensity at 1405 cm^{-1} corresponded to NH_4^+ bending vibration (Nakamoto, 1997), and the presence of CuCl_4^{2-} could be confirmed by asymmetric stretching vibrations at 435 cm^{-1} (Amirthaganesan, Kandhaswamy, & Srinivasan, 2005).

It has already been reported that the band characteristic of N–H stretching vibration in the FT-IR spectra of ammonium salts showed multiple splitting with strong hydrogen bonding, while its absence led to a fusion of that band into a single peak (Choi & Larrabee, 1989). Such changes in the N–H stretching region, resulting from either microwave irradiation or convectional heating,

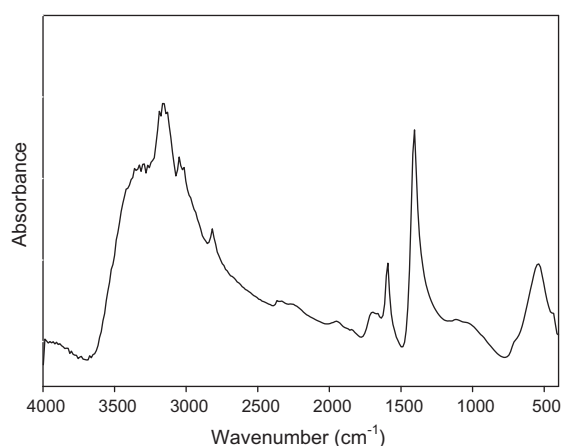


Fig. 4. FT-IR spectrum of ATCl-Cu.

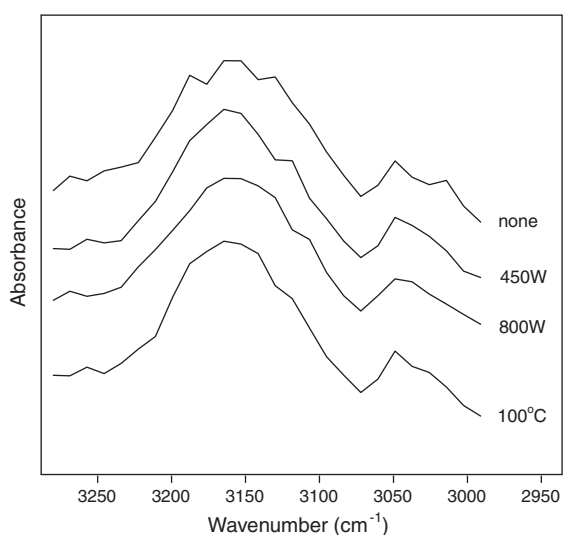


Fig. 5. FT-IR spectra in the range 3300–2900 cm^{-1} of ATCl-Cu: unmodified (none) and either microwave irradiated (450 or 800 W) or convectionally heated (100 °C).

were detected in the spectra of ATCl-Cu (Fig. 5). The broad absorption band centered at 3160 cm^{-1} exhibited shoulders at 3310 and 3049 cm^{-1} in the spectrum of salt prior to its microwave

irradiation or convectional heating, while a single broad peak was observed in the spectrum of salt after its irradiation or heating. The changes in CuCl_4^{2-} geometry under reaction conditions could, therefore, affect the reactivity of starch.

The spectra of all the starch cuprate samples showed a similar pattern. To reveal any changes in the functional groups of starch (Table 4) that were induced by the process of cupration, an analysis of the patterns of the difference bands was carried out. An example of the differential spectrum is shown in Fig. 6.

In the spectrum of starch cuprate an increase in the absorption in the region between 3700 and 3100 cm^{-1} (ν_{OH} of the water molecules) and an enhancement of the band at 1640 cm^{-1} (δ_{OH} of the water molecules) were noted (Fig. 6a). These changes were accompanied by an increased intensity in the difference band at 3440 and 1636 cm^{-1} . Thus, it confirmed that water was involved in the formation of starch cuprate. The Cu(II) coordination sphere was known to be very flexible, and one could assume for the CuCl_4^{2-} either $4+1$ or $4+2$ coordination due to sufficient strength of the N–H–Cl hydrogen bonds between cation and CuCl_4^{2-} (Willett, Haugen, Lebsack, & Morrey, 1974). Thus, the cuprate anion introduced into potato starch apparently coordinated the water molecules from the hydrated spaces located in amorphous part of granules (Blennow et al., 2006; Szymońska, Wieczorek, Molenda, & Bielańska, 2008; Łabanowska, Bidzińska, Dyrek, & Szymońska, 2006; Śmigielńska & Lewandowicz, 2007). At elevated temperatures, when the N–H–Cl hydrogen bonds weakened, the hydrogen bond interactions between the hydroxyl groups of the D-Glc and chlorine atoms of introduced cuprate anion became essential for that coordination.

An increased intensity in the difference band at 1024 cm^{-1} , and a decreased band at 968 cm^{-1} , could also be observed in the difference spectrum (Fig. 6b). Moreover, the band in the spectrum of native starch originally at 982 cm^{-1} decreased and moved to 991 cm^{-1} . Since that band is related to hydrogen bonding of the hydroxyl groups at C-6 (Van Soest, de Wit, Tournois, & Vliegert, 1994), the 9 cm^{-1} shift of that band towards higher wave numbers confirms that the involvement of these hydroxyl groups in intra- and inter-molecular hydrogen bonding changed as a result of cupration. The difference spectrum exhibited additionally two bands at 458 and 423 cm^{-1} (Fig. 6b), which based on the ATCl-Cu spectrum (Fig. 4 and Table 4) could be assigned to the CuCl_4^{2-} , which were evidently incorporated by the cupration procedure into starch. The pattern of this part of the spectrum differed from the pattern of ATCl-Cu. Therefore, the changes in the hydrogen bonding of the hydroxyl groups should be a result of the ligand exchange reaction, i.e. the hydroxyl ligand of D-Glc of starch replaced the chloride ligand of ATCl-Cu.

Table 4
Band assignment in the FT-IR spectra of native starch and ammonium tetrachlorocuprate(II).

Native starch		Ammonium tetrachlorocuprate(II)	
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	3190 sh, 3160 vs 3130 sh	νNH_4^+
2928 m	ν_{CH}	2820	νNH_4^+
1648 w	δ_{OH} polymer bound water	1590 m	asymmetric $\delta_{\text{NH}_4^+}$
1432 m	$\delta_{\text{OH}}, \delta_{\text{CH}}$	1405 s	$\delta_{\text{NH}_4^+}$
1377 m	$\delta_{\text{OH}}, \delta_{\text{CH}}$	540 m	Librational modes of water and NH_3 group
1162 s	$\nu_{\text{C-C}}, \nu_{\text{C-O}}, \delta_{\text{C-OH}}$	435 w	Asymmetric ν_{CuCl_4}
1082 s	$\delta_{\text{C-O-C}}$ α -1,4 glycosidic linkage		
982 vs	$\delta_{\text{C-OH}}$		
929 m	$\delta_{\text{C-O-C}}$ α -1,4 glycosidic linkage		
859 w	$\nu_{\text{C-O-C}}$ glycosidic linkage		
765 w	$\nu_{\text{C-C}}$		

^a Notation of the band intensity is as follows: vs – very strong, s – strong, m – medium, w – weak, sh – shoulder.

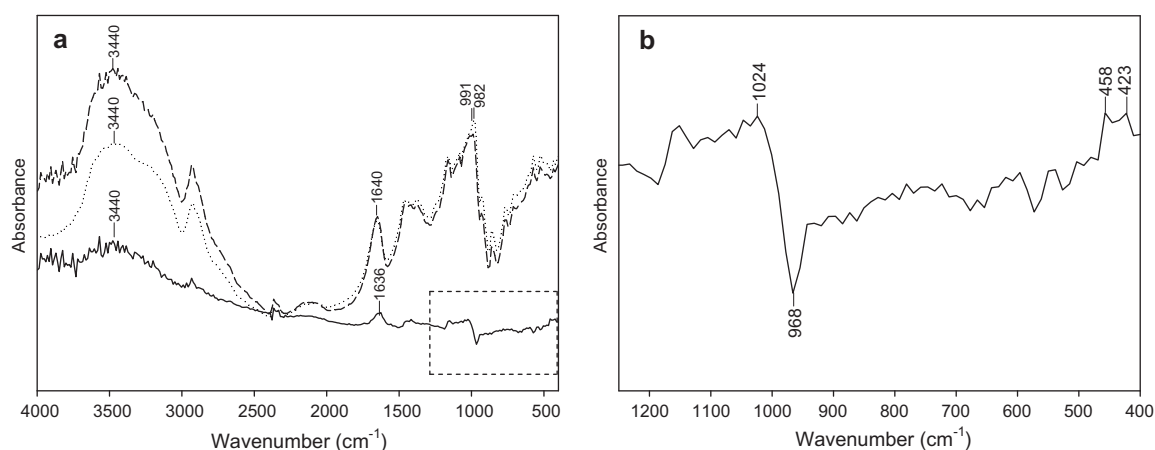


Fig. 6. FT-IR spectra in the range 4000–400 cm^{-1} of the native potato starch (---), potato starch blended with ATCI-Cu at proportion 1:1 and microwave irradiated with 800 W (- - -) and the differential spectrum of the latter, from which the spectrum of the native potato starch was subtracted (—) (a). Differential spectrum in the range narrowed down to 1300–400 cm^{-1} (b).

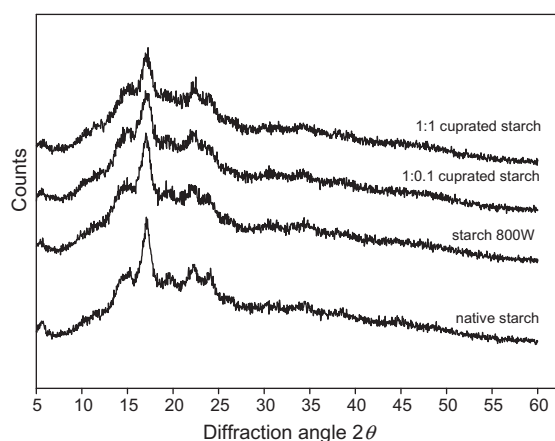


Fig. 7. Powder X-ray diffractograms of potato starch prior to and after microwave irradiation with 800 W, and the cupration products resulting from microwave irradiation with 800 W of 1:0.1 and 1:1 potato starch:ATCI-Cu blends.

3.2. Physicochemical characteristics of starch cuprate

Upon microwave irradiation and the convectional heating of starch, the corresponding X-ray patterns turned more flat, and

Table 5
The onset (T_o), peak (T_p), and conclusion (T_c) temperatures and enthalpy change (ΔH) during gelatinisation of potato starch and its cuprated derivatives.^a

Treatment	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Starch				
None	54.7 ± 0.1 ^f	65.2 ± 0.1 ^{b,c}	82.0 ± 0.0 ^b	13.4 ± 0.2 ^f
Microwave irradiation at 450 W 8 min	54.0 ± 0.1 ^{e,f}	65.3 ± 0.9 ^{b,c}	81.0 ± 0.9 ^b	13.0 ± 0.4 ^{e,f}
20 min	53.0 ± 1.1 ^{d,e}	63.1 ± 1.0 ^a	81.0 ± 0.8 ^b	13.0 ± 0.0 ^{e,f}
Microwave irradiation at 800 W 3 min	54.0 ± 0.2 ^{e,f}	64.4 ± 0.4 ^b	82.0 ± 0.9 ^b	13.1 ± 0.1 ^{e,f}
Convectional heating at 100 °C	54.0 ± 0.2 ^{e,f}	64.9 ± 0.1 ^{b,c}	77.0 ± 1.6 ^a	13.0 ± 0.3 ^{e,f}
Starch:ATCI-Cu = 1:0.1				
Microwave irradiation at 450 W 8 min	49.0 ± 0.3 ^a	67.4 ± 0.2 ^f	82.0 ± 0.8 ^b	8.6 ± 0.6 ^b
Microwave irradiation at 800 W 3 min	52.0 ± 0.2 ^{c,d}	66.2 ± 0.1 ^{d,e}	80.0 ± 1.6 ^b	10.2 ± 0.1 ^c
Convectional heating at 100 °C	54.0 ± 0.3 ^{e,f}	67.0 ± 0.2 ^{e,f}	77.0 ± 0.8 ^a	12.2 ± 0.1 ^{d,e,f}
Starch:ATCI-Cu = 1:1				
Microwave irradiation at 450 W 20 min	51.0 ± 0.2 ^{b,c}	67.1 ± 0.1 ^{e,f}	82.0 ± 0.8 ^b	11.0 ± 0.2 ^{c,d}
Microwave irradiation at 800 W 3 min	51.5 ± 0.6 ^{c,d}	65.5 ± 0.1 ^{c,d}	77.0 ± 0.0 ^a	6.2 ± 0.8 ^a
Convectional heating at 100 °C	50.0 ± 0.2 ^{a,b}	67.8 ± 0.2 ^{e,f}	82.0 ± 0.3 ^b	12.1 ± 0.1 ^e

^a Results are expressed as means of three measurements ± standard deviation. The values in the columns marked with various letters differ significantly ($p < 0.05$).

the phase transition enthalpy (ΔH) slightly decreased. That trend agreed with observations in previous studies (Staroszczyk, 2009a, 2009b; Staroszczyk & Janas, 2010a, 2010b; Staroszczyk et al., 2007) and reflected some disorder of the crystalline structure of the starch granule introduced by processing (Fig. 7, Table 5).

The reduced intensity of the characteristic diffraction peaks of B-type crystalline structure, at 5.8°, 14.9°, 17.0°, 19.6°, 22.2° and 24.0° 2θ , as well as the decrease in the ΔH values, indicated that the cupration partly deteriorated the crystalline structure of starch. However, while the ΔH values of starch subjected solely to microwave irradiation dropped in the same degree as starch was subjected to convectional heating, the ΔH values of starch cuprate in the microwave-assisted reaction decreased more than those in starch cuprate from convectional heating. In contrast to the reaction performed by convectional heating, the results of the microwave assisted reaction were also ATCI-Cu concentration dependent. As a consequence, the products from the microwave irradiation bound more water and were more water-soluble (Table 6).

The phase transition temperature (T_p) of starch processed without ATCI-Cu slightly decreased. However, the T_p of starch cuprates increased, not only with respect to irradiated or heated starch, but also to native starch. It could confirm that the cupration of starch with ATCI-Cu was favourable for the hydrogen bond formation,

Table 6

Water binding capacity (WBC) and aqueous solubility (AS) of potato starch and its cuprated derivatives.^a

Treatment	WBC (g/g)	AS (%)
<i>Starch</i>		
None	9.13 ± 1.10 ^a	1.00 ± 0.06 ^b
Microwave irradiation at 450 W 8 min	18.03 ± 2.11 ^b	0.01 ± 0.00 ^a
20 min	92.83 ± 12.04 ^c	0.11 ± 0.01 ^a
Microwave irradiation at 800 W 3 min	14.27 ± 1.24 ^b	0.01 ± 0.00 ^a
Convictional heating at 100 °C	18.50 ± 2.34 ^b	0.02 ± 0.00 ^a
<i>Starch:ATCl-Cu = 1:0.1</i>		
Microwave irradiation at 450 W 8 min	9.35 ± 0.86 ^a	10.31 ± 0.40 ^e
Microwave irradiation at 800 W 3 min	7.64 ± 1.15 ^a	5.87 ± 0.24 ^d
Convictional heating at 100 °C	8.82 ± 0.99 ^a	3.24 ± 0.35 ^c
<i>Starch:ATCl-Cu = 1:1</i>		
Microwave irradiation at 450 W 20 min	18.33 ± 2.20 ^b	3.73 ± 0.32 ^c
Microwave irradiation at 800 W 3 min	15.16 ± 1.98 ^b	7.52 ± 0.35 ^d
Convictional heating at 100 °C	8.75 ± 1.01 ^a	2.39 ± 0.27 ^c

^a Results are expressed as means of 10 measurements ± standard deviation. The values in the columns marked with various letters differ significantly ($p < 0.05$).

although it was accompanied by disorder of its crystalline structure.

Data in Table 6 show that regardless the power applied, when lower dose of ATCl-Cu was applied, the microwave-assisted cupration of starch resulted in the products of reduced WBC and increased AS. The starch cuprated with a higher dose of ATCl-Cu bound more water and was in most cases less water-soluble. The values of WBC and AS of the starch cuprated by convectional heating did not depend on the concentration of ATCl-Cu, and after an initial decrease of WBC and an increase of AS, remained almost unchanged. Likely, as the microwave-assisted cupration progressed, the starch became polar, which could enhance its ability to bind water, and facilitate swelling of starch. As a consequence, the crystalline regions were partially degraded.

4. Conclusions

Ammonium tetrachlorocuprate(II) esterified starch both in the microwave-assisted and the convectional heating process, in which the ligand exchange participated. The microwave-assisted reaction significantly accelerated cupration. The cupration reduced starch crystallinity.

Acknowledgement

The author is grateful to Prof. Piotr Tomasik from the University of Agriculture in Cracow, Poland, for his constructive remarks that have helped to improve the manuscript.

References

- Amirthaganesan, G., Kandhaswamy, M. A., & Srinivasan, V. (2005). Synthesis and characterization of dihydroxylammonium tetrachlorocuprate dehydrate crystals. *Crystal Research and Technology*, 40, 593–596.
- Blennow, A., Houborg, K., Andersson, R., Bidzińska, E., Dyrek, K., & Łabanowska, M. (2006). Phosphate positioning and availability in the starch granule matrix as studied by EPR. *Biomacromolecules*, 7, 965–974.
- Bindzus, W., Altieri, P. A., Kasic, J. J., Trzasko, P. T. (2002). Starch phosphate ester composition, process and method of use in food. *European Patent Application*. Pat. No. 1179543.
- Choi, S., & Larrabee, J. A. (1989). Thermochromic tetrachlorocuprate(II). *Journal of Chemical Education*, 66, 774–776.
- Ciesielski, W., Lii, C.-Y., Yen, M.-T., & Tomasik, P. (2003). Interactions of starch with salts of metals from the transition groups. *Carbohydrate Polymers*, 51, 47–56.
- Ciesielski, W., & Tomasik, P. (2003a). Thermal properties of complexes of amaranthus starch with selected metal salts. *Thermochimica Acta*, 403, 161–171.
- Ciesielski, W., & Tomasik, P. (2003b). Coordination of cassava starch to metal ions and thermolysis of resulting complexes. *Bulletin of the Chemical Society of Ethiopia*, 17, 155–165.

- Ciesielski, W., & Tomasik, P. (2004a). Werner-type metal complexes of potato starch. *International Journal of Food Science and Technology*, 39, 691–698.
- Ciesielski, W., & Tomasik, P. (2004b). Metal complexes of amylose and amylopectins and their thermolysis. *Journal of Inorganic Biochemistry*, 98, 2039–2051.
- Fukuda, Y. (2007). What is chromotropism. In Y. Fukuda (Ed.), *Inorganic chromotropism: Basic concepts and applications of colored materials* (pp. 11–40). Berlin: Springer-Verlag.
- Fortuna, T. (1998). The properties of distarch phosphates and retrogradation of their pastes. *Polish Journal of Food and Nutrition Sciences*, 7(1), 35–40.
- 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.
- Johnson, M. A., & Gratzek, J. M. (1986). Influence of sucrose and starch on the development of anemia in copper- and iron-deficient rats. *The Journal of Nutrition*, 116, 2443–2452.
- Judd, M. D., Plunkett, B. A., & Pope, M. I. (1975). The structures and thermal decomposition of cupric mono, di and trichloroacetates. *Journal of Thermal Analysis*, 9, 83–92.
- Leszczyński, W. (1985). Properties of potato starch saturated with ferric salts. *Acta Alimentaria Polonica*, 11, 21–34.
- Lewandowicz, G., Szymańska, G., Voelkel, E., & Walkowski, A. (2000). Food grade starch phosphates obtained by microwave radiation – Structure and functionality. *Polish Journal of Food and Nutrition Science*, 9(3), 31–37.
- Łabanowska, M., Bidzińska, E., Dyrek, K., & Szymańska, J. (2006). Electron paramagnetic resonance study of water distribution in starch granules. *Biopolymers*, 82, 549–557.
- 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.
- Nakamoto, K. (1997). *Infrared and Raman spectra of inorganic and coordination compounds. Part A: Theory and applications in inorganic chemistry* (5th ed.). New York: J. Wiley and Sons Inc.
- PN-EN ISO 3188 Standard, 2000. Starches and derived products. Determination of nitrogen content by the Kjeldahl method. Titrimetric method.
- Penfield, K. W., Gewirth, A. A., & Solomon, E. I. (1985). Electronic structure and bonding of the blue copper site in plastocyanin. *Journal of the American Chemical Society*, 107, 4519–4529.
- Pickart, L. R. (1999). Starch–metal complexes for skin and hair, US Patent Office. Pat. No. 5858993.
- Richter, M., Augustat, S., & Schierbaum, F. (1968). *Ausgewählte methoden der stärkechemie*. Leipzig: VEB Fachbuch Verlag.
- Śmigielńska, H., & Lewandowicz, G. (2007). Functional properties of the modified starches fortified by copper ions. *Żywność Nauka Technologia Jakość*, 6, 198–209.
- Śmigielńska, H., Lewandowicz, G., Goslar, C., & Hoffmann, S. K. (2005). Binding of the trace elements: Cu(II) and Fe(III) to the native and modified nutritive potato starches studied by EPR. *Acta Physica Polonica A*, 108, 303–310.
- 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, W., Janas, P., Tomasik, P. (2007). Microwave-assisted solid-state sulphation of starch. *e-Polymers* No. 140.
- Staroszczyk, H., & Janas, P. (2010a). Microwave-assisted synthesis of zinc derivatives of potato starch. *Carbohydrate Polymers*, 80, 962–969.
- Staroszczyk, H., & Janas, P. (2010b). Microwave-assisted preparation of potato starch silicated with silicic acid. *Carbohydrate Polymers*, 81, 599–606.
- 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.
- Stern, E. (1926). Improvements in and relating to processes of making starch products and dry starch products. GB Patent. Pat. No. 272274.
- Szymańska, J., Wieczorek, J., Molenda, M., & Bielańska, E. (2008). Uptake of Cu²⁺ by starch granules as affected by counterions. *Journal of Agricultural and Food Chemistry*, 56, 4054–4059.
- Tomasik, P., Anderegg, J. W., Baczkowicz, M., & Jane, J. (2001). Potato starch derivatives with some chemically bound bioelements. *Acta Polonicae Pharmaceutica. Drug Research*, 58, 447–452.
- Tomasik, P., & Schilling, C. H. (2004). Chemical modification of starch. *Advances in Carbohydrate Chemistry and Biochemistry*, 59, 176–404.
- Tomasik, P., Schilling, Ch. H., Anderegg, J. W., & Refvik, M. (2000). Starch–lanthanum complexes. *Carbohydrate Polymers*, 41, 61–68.
- Tyrlík, S. K., Tomasik, P., Anderegg, J. W., & Baczkowicz, M. (1997). Titanium (IV) starch complexes. *Carbohydrate Polymers*, 34, 1–7.
- Van Soest, J. J. G., de Wit, D., Tournois, H., & Vliegthart, J. F. G. (1994). Retrogradation of potato starch as studied by Fourier transform infrared spectroscopy. *Starch/Stärke*, 46, 453–457.
- Willett, R. D., Haugen, J. A., Lebsack, J., & Morrey, J. (1974). Thermochromism in copper(II) chlorides. Coordination geometry changes in CuCl₄²⁻ anions. *Inorganic Chemistry*, 13, 2510–2513.
- 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).