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Air oxidation of potato starch over Cu(II) catalyst

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Abstract

Cu(II) ions catalyzed the air oxidation of starch. The formation of carbonyl derivatives was favored over the oxidation to starch carboxylates. Catalyzing Cu(II) ions could not be removed from the product due to formation of complexes with starch and copper(II) carboxylates. Resulting copper derivatives were less thermally stable than that of original starch. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Potato starch; Cu(II) catalyst; Oxidation

1. Introduction

There are several methods of starch oxidation, which result in the formation of carbonyl and/or carboxylic starch as well as starch dialdehyde (Tomasik & Schilling, 1999). Oxidation may proceed either on the granule surface or in its interior. Our recent paper (Bala-Piasek & Tomasik, 1999) described oxidation of potato starch with air over ammonium vanadate (V) taken as the catalysts. The oxidation provided carbonyl as well as carboxylic starch. It proceeded on the granule surface. There are several metal ions, which potentially can catalyze starch oxidation. In this paper oxidation of starch over Cu(II) catalyst is presented. Since the Cu(II) catalyst resided in solution in the ionized form the method presented could potentially be suitable for one step synthesis of copper(II) carboxylates of starch.

2. Materials and methods

2.1. Materials

Potato starch was isolated in 1998 in Potato Enterprise in Lomza (Poland). Copper(II) sulfate was delivered by Polish Chemicals, POCh Gliwice. Water was re-distilled.

2.2. Methods

2.2.1. Starch aeration

In a round bottom flask potato starch (50 g) was placed together with re-distilled water (500 cm^3) and $CuSO_4 \cdot 5H_2O$ (3.12, 7.81, 15.62 or 31.24 g). The suspension was agitated at room temperature. After 15 min 10% aq. NaOH was added on stirring until pH of the suspension increased to 9.0 ± 0.2. A further 48 h agitation at 35–40°C was accompanied by passing of slow stream of the air. Since in this period pH decreased to 7.0 a subsequent volume of 10% aq. NaOH was added to rise pH to 9.0. After 48 h reaction mixture was filtered and rinsed on the filter with re-distilled water (1000 cm^3). The product was dried in the air. The control samples were prepared analogously but without aeration.

2.2.2. Analyses

Carboxylic and carbonyl groups were determined according to Boruch (1970) and Krajcinovic (1948), respectively. Aqueous solubility and water binding capacity was determined according to Richter, Augustat and Schierbaum (1969). Estimations were corrected.

Characteristics of gelation were carried out for 7.2% aqueous starch suspensions using the Brabender viscograph and following the standard program, i.e. rotor velocity was 75 rpm, rate of temperature increase from 20 to 96°C was 1.5°C/min. Then the gel was maintained on stirring for 20 min at 96°C followed by cooling to 50°C with the 1.5°C rate of the temperature decrease.

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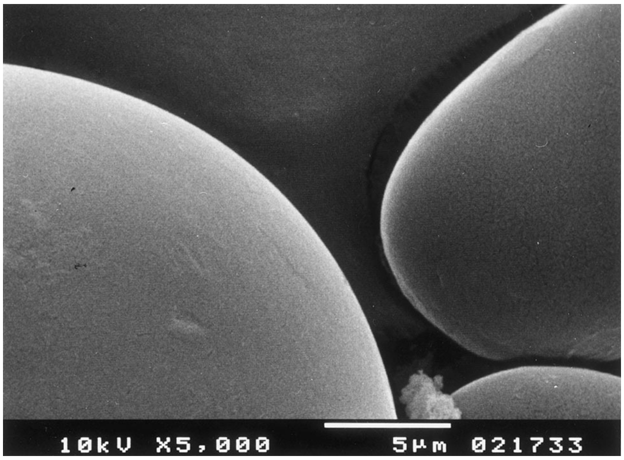

Fig. 1. Micrograph ($10^4\times$ magnification) of starch granule treated with copper catalyst and non-aerated.

Electron micrographs were taken with a JEOL 5400 instrument equipped with a LINK ISIS 300 Oxford Instruments electron probe energy dispersive microanalyzer. Samples were fixed to the holder with two-side carbon type and covered with gold. The granule morphology was studied up to $10^4\times$ magnification employing secondary electrons at an accelerating gradient of 20 eV.

Thermal analysis (thermal gravimetry (TG), differential thermal gravimetry (DTG) and differential thermal analysis (DTA)) was run on 200 mg samples in the air over the range 20–500°C with a temperature gradient of 10°C/min. Corrundum 8 μm was the standard. The computerized Paulik-Paulik Erdey Q-1500D instrument (Hungary) was used. Copper content in aerated starch was determined using the AAS technique at 324.8 nm.

3. Results and discussion

Fig. 1 presents surface of starch granules treated with $CuSO_4$ prior to air oxidation and thoroughly washed with distilled water in order to eliminate the catalyst. In spite of thorough washing of the sample one may see a small deposit of $CuSO_4$ in a capillary between starch granules. Some copper content could also result from the formation of starch–copper complexes (Tomasik & Schilling, 1998). Copper reagent did not digest granule surface. The residual copper could also be recognized in the metal analysis on the granule surface (Fig. 2). The aeration of starch in the presence of the copper catalyst produced erosion of the granule surface as seen in Fig. 3a–d The degree of erosion was independent of the amount of the copper catalyst, which increased from 2 to 20 g per 100 g of starch, respectively. Fig. 4 shows that the degree of the surface destruction is independent of the granule size. Starch granules aerated even at the lowest, 2 g/100 g of starch, concentration of the catalyst colored blue and this color could not be removed by intensive washing with water. Scanning of the granule surface confirmed copper residing thereon (Fig. 5). Copper ions were taken by oxidized starch from solution and it could reside in granules in the form of complexed $CuSO_4$ and/or as the copper carboxylate. The estimated

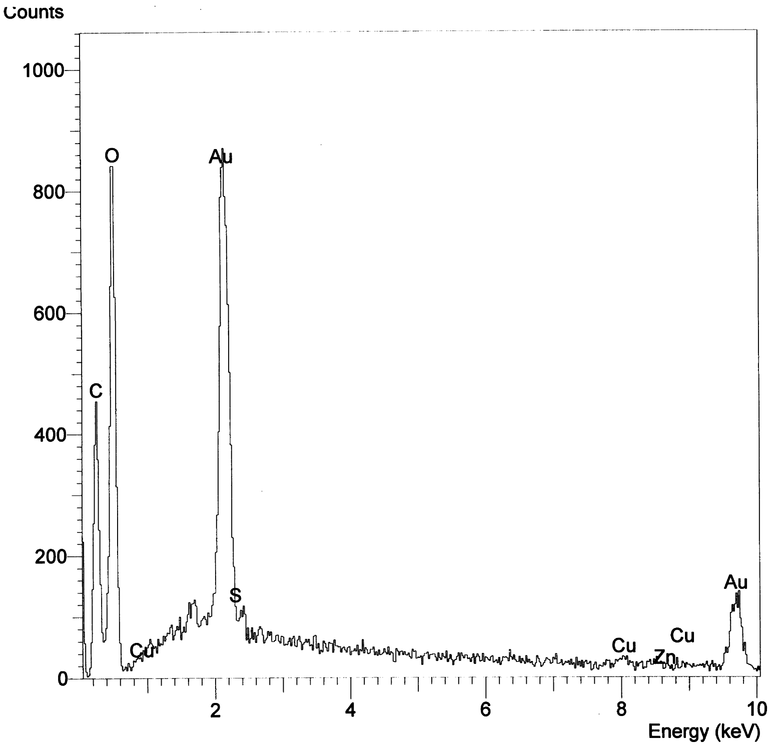

Fig. 2. Elemental composition of the surface of starch granule after blending starch with copper catalyst then rinsed with distilled water.

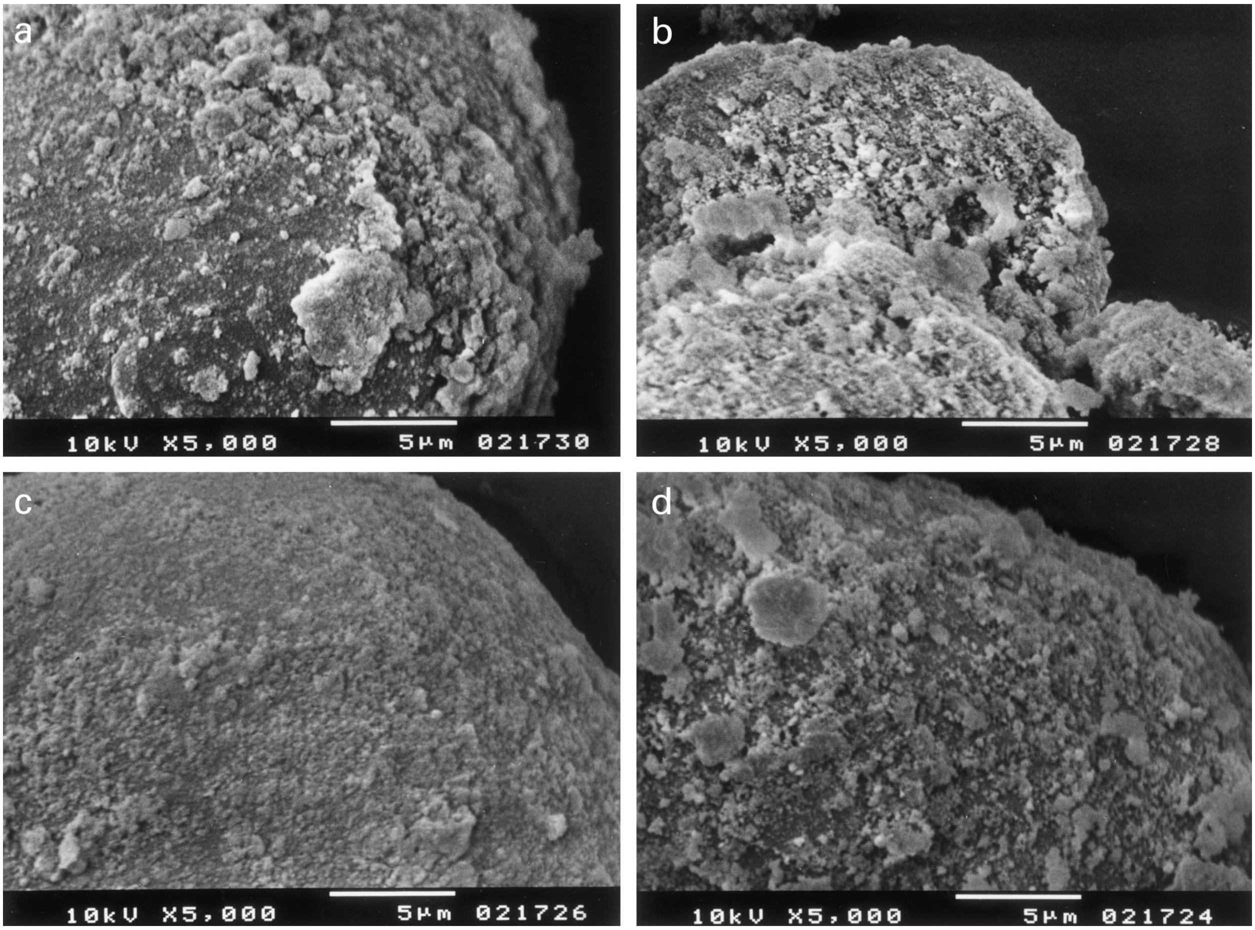

Fig. 3. Micrographs ($10^4\times$ magnification) of starch granule treated with varying doses of the copper catalyst. Amount of the Cu(II) catalyst was: (a) 2, (b) 5, (c) 10, and (d) 20 g.

copper content using the atomic absorption spectrometry gave the following results; starch soaked in aqueous solution of $CuSO_4$ and not aerated contained only 1.16 ppm of copper. Aerated samples contained 2.0, 4.3, 6.0 and 11.0% of copper in the samples aerated in 3.12, 7.81, 15.62, and 31.24 g of $CuSO_4{\cdot}5H_2O$ per 50 g of starch, respectively. These results strongly suggest the formation of copper carboxylates. Residual amount of the catalyst left in the reaction product can seriously influence estimations of the degree of oxidation. Under such circumstances estimations of the carbonyl and carboxyl groups by common methods would be obscured. Several authors who estimated the content of carbonyl groups in starch oxidized in the presence of copper could come to wrong conclusions when they applied the Smith (1967) and Krajcinovic (1948) methods, which involved hydroxylamine. One of the possible examples could be delivered by Parovouri, Hamunen, Forsell, Autio and Poutanen (1995) who oxidized starch with hydrogen peroxide in the presence of Fe(III) and Cu(II). In the referred case the estimations could also be obscured by H_2O_2 potentially complexed by starch.

Changes in aqueous solubility on the oxidation of starch (Table 1) additionally to the microscopic evidence, support the conclusion that starch underwent oxidation and resulting starch carboxylate hold Cu(II) not only in the form of sparingly soluble copper salt but also as sparingly water soluble copper complexes. Addition of low doses of $CuSO_4$ to starch decreased the solubility of the latter even when it was not aerated. However, higher doses of $CuSO_4$ increased

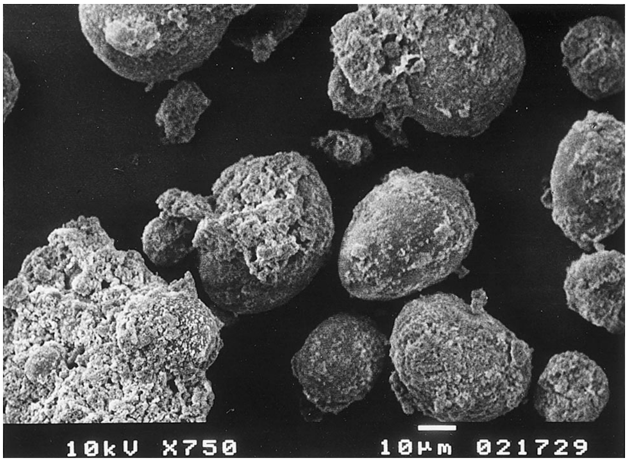

Fig. 4. Erosion of the surface of starch granules of varying size.

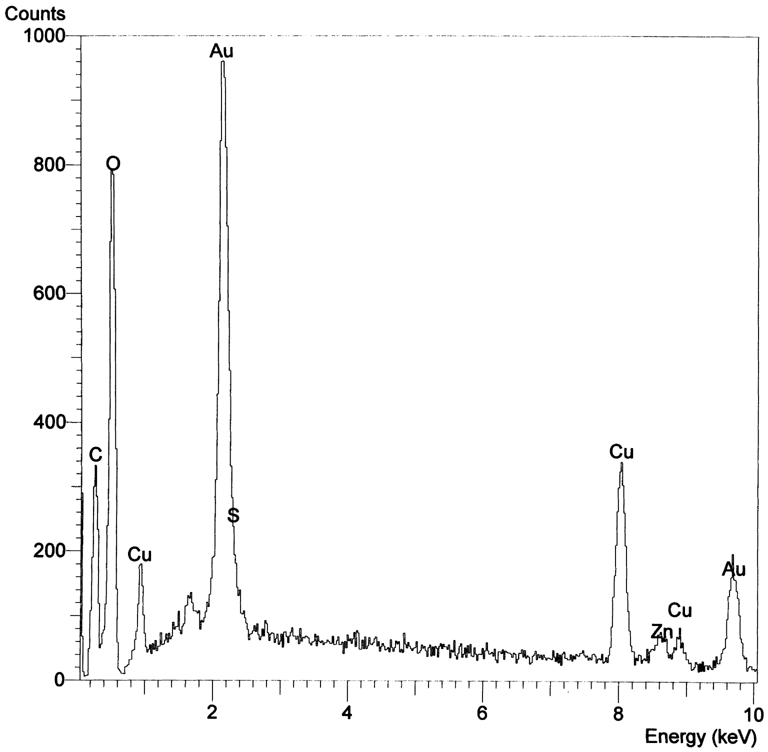

Fig. 5. Elemental composition of the surface of granule aerated over 2 g of Cu(II) catalyst then rinsed with water.

Table 1
Aqueous solubility (AS) (%) and water binding capacity (WBC) (g/g of dry sample) of starch aerated over varying amount of Cu(II) catalyst (A) and non-aerated samples blended with the same amount of Cu(II) catalyst (N) as the secondary control

Amount of Cu(II) catalyst (g)		25°C[a]		40°C[b]		60°C[c]	
		AS	WBC	AS	WBC	AS	WBC
0 (primary control)	N	0.91	0.87	1.79	0.90	7.55	12.91
2	A	0.0	1.46	0.0	1.43	1.21	5.00
	N	0.0	1.54	0.0	1.38	0.89	6.31
5	A	1.23	1.98	0.91	1.85	2.58	4.25
	N	0.0	1.49	0.0	1.59	1.30	6.17
10	A	0.96	1.96	0.68	1.83	1.60	5.97
	N	0.75	1.78	0.60	1.97	2.13	6.59
20	A	1.52	1.83	0.84	2.03	1.25	4.38
	N	1.75	1.56	1.68	1.95	2.60	4.61

[a] Average deviations for AS and WBC are 6.96 and 0.83%, respectively, and standard deviations $s = 0.08588$ and 0.01634, respectively.

[b] Average deviations for AS and WBC are 10.00 and 4.11%, respectively, and $s = 0.1825$ and 0.0849, respectively.

[c] Average deviations for AS and WBC are 14.1 and 13.76%, respectively, and $s = 0.1919$ and 0.3538, respectively.

solubility of the aerated and non-aerated material. Thus, one may accept that first smaller doses of $CuSO_4$ formed insoluble complexes, presumably coordination complexes. In no case formation of either copper metal or copper (I) oxide could be noted. Thus, starch was passive to the oxidation by Cu(II) ions under neutral conditions. Water binding capacity of starch increased after the addition of $CuSO_4$ possibly reflecting the ability of copper sulfate and carboxylate towards hydration.

Determination of the carboxylic groups in the aerated product was performed according to Smith (1967). Results

Table 2
Content of carboxylic groups, *C*, and Cu in starch aerated over Cu(II) catalyst

Amount of Cu(II) catalyst (g)	*C* (mval/100 g of dry sample)	Cu (%)
0 (control)	4.11	1.16[a]
2	3.95	2.0
5	4.00	4.3
10	4.56	6.0
20	n.e[b]	11.0

[a] This value is give in ppm.

[b] Not estimated.

Table 3
Content of the carbonyl groups, *Z*, in starch aerated over varying amounts of Cu(II) catalyst and in non-aerated starch combined with the same amount of the Cu(II) catalyst

Amount of Cu(II) catalyst (g)	*Z* (mval/100 g of dry sample)		
	Aerated starch	Non-aerated starch	Δ
0 (primary control)		2.32	
0 (pH 9.0)	20.52	18.54	1.98
2	136.52	113.52	23.0
5	226.91	199.80	38.11
10	273.60	226.70	46.9
20	390.75	380.14	106.1

Table 4
Brabender characteristics of gelation of starch aerated over varying amount of Cu(II) catalyst (A) and non-aerated starch blended with the same amount of Cu(II) catalyst (N)

Amount of Cu(II) catalyst (g)		Gelation beginning (°C)	η_{max} (B.u)	η_{max} after 20 min at 96°C (B.u)	η_{min} (B.u)	Temp. at η_{min} (°C)	η after cooling to 50°C (B.u)
0		65.5	1250	850	830	87.0	1330
2	A	61.0	960	810	760	84.0	1270
	N	61.0	730	570	530	85.0	890
5	A	62.5	550	510	490	88.0	860
	N	59.5	580	510	495	90.0	950
10	A	62.5	660	620	610	90.0	1080
	N	61.0	450	410	405	91.5	850
20	A	64.0	280	260	255	90.0	485
	N	64.0	200	185	180	88.5	310

presented in Table 2 showed that the number of carboxylic groups increased with the amount of CuSO$_4$ added. The number of carbonyl groups dramatically rose by one order of magnitude after the addition of copper sulfate (Table 3). Evidently such high figures are due to consumption of hydroxylamine by Cu(II) ion. However, difference in the consumption of hydroxylamine by aerated and non-aerated samples showed that Cu(II) ion catalyzed the oxidation of starch to the carbonyl derivatives rather than to the carboxylates.

An inspection of the Brabender characteristics of gelation (Table 4) showed that Cu(II) ion reduced the viscosity maximum and minimum, as well as viscosity after 20 min. at 96°C and after cooling to 25°C with respect to these parameters in control sample. Viscosity maxima for aerated samples were always higher than for non-aerated samples. They decreased in a parallel manner with the increase in the copper sulfate concentration. It might be an evidence for a weak oxidation of starch to carboxylates, which by bonding of Cu(II) ion produced a random crosslinking. Viscosity after 20 min at 96°C, viscosity minimum, and viscosity after cooling to 25°C exhibited a similar trend but there were weak extrema on the dependence of these parameters on the concentration of the copper salt. Such extrema appeared at the concentration level of 5–10 g of CuSO$_4$. In characteristics of gelation for starch aerated over V (V) catalyst (Bala-Piasek & Tomasik, 1999) anomalies appeared in the same range of the concentration of the vanadium catalyst used. However, contrary to the present case they were minima. Temperatures at the viscosity minimum varied insignificantly.

Thermal analysis of aerated samples revealed that thermal stability and water binding capacity of aerated products

Table 5
Thermal characteristics of starch and its selected copper derivatives

Original starch	TG[a]: 57; 150; 268 (−5%); 310 (−26%) DTG[b]: 100; 288 DTA[c]: 108; 275; 340; 380s
Starch oxidized over 10 g of CuSO$_4$	TG[a]: 65; 145; 258 (−4%); 265 (−20%); 335 (−25%); 410 (−30%) DTG[b]: 100; 258 DTA[c]: 100; 258; 280s; 295; 329
Starch oxidized over 20 g of CuSO$_4$	TG[a]: 65; 140; 245 (−5%); 252 (−7.5%); 265 (−16%) DTG[d]: 105; 240s, 252; 318 DTA[c]: 105; 252; 280

[a] In °C. In parentheses weight loss is given from the origin up to the specified temperature. After last temperature reported there is a monotonous decrease of the sample weight.

[b] In °C. Both effects are endothermic. First flat minimum is due to water loss, the second is related to the polysaccharide decomposition.

[c] In °C. Shoulders are denoted by “s”.

[d] In °C. The main decomposition peak is preceded by a shoulder, which can represent a glassy transition in the material.

were lower than these for unprocessed starch and decreased with the amount of Cu(II) catalyst added (Table 5).

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