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Starch dialdehyde from potato starch illuminated with linearly polarized visible light

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ABSTRACT

Prior to the oxidation with iodate(VII), potato starch was 24 h illuminated with linearly polarized visible light. The illumination provided starch dialdehyde of higher aqueous solubility and much higher susceptibility to enzymatic hydrolysis with glucoamylase. It could be rationalized in terms of the effect of illumination on the macrostructure of starch granules as shown with scanning electron microscope (SEM) and X-ray powder diffraction (XRD) studies.

1. Introduction

Effect of illumination with linearly polarized visible light (LPVL) upon the structure and properties of starch was described by Fiedorowicz, Lii, and Tomasik (2002), Fiedorowicz and Khachatryan (2004), Staroszczyk, Fiedorowicz, and Tomasik (2007). In non-enzymatic processes, LPVL de-branched starch amylopectin inside starch granules and caused repolymerization of cut off short branches into linear amylose-like polysaccharide. LPVL activated enzymes present inside starch granules causing hydrolysis of starch (Navez & Rubenstein, 1928). LPVL also activated particular enzymes suitable for transformations of polysaccharides. Thus, enzymatic hydrolysis of starch (Fiedorowicz & Chaczatrian, 2003), xylan (Konieczna-Molenda, Fiedorowicz, Lai, & Tomasik, 2008), chitin and chitosan (Konieczna-Molenda, Fiedorowicz, Zhong, & Tomasik, 2008), as well as increased production of cyclodextrins with cyclodextrin glycosyltransferase (Fiedorowicz, Konieczna-Molenda, Khachatryan, & Tomasik, 2006) could be stimulated with LPVL.

Starch dialdehyde (DAS) (Para, Karolczyk-Kostuch, Hajdon, & Tomasik, 2000; Veelaert, Polling, & de Wit, 1994) has several industrial applications and has considerable further industrial potential (Kanth et al., 2006; Tomasik & Schilling, 2004). Therefore, checking possible effect of LPVL upon starch prior to its oxidation upon properties of resulting DAS seemed to be interesting.

In this study, potato starch illuminated for 24 h with LPVL was oxidized with sodium iodate(VII) to DAS with electrolytic regeneration of the periodate ions. The effect of illumination was evaluated by a comparison of degree of oxidation, aqueous solubility and rate of enzymatic hydrolysis with glucoamylase of DAS from illuminated and non-illuminated starch.

2. Materials and methods

2.1. Materials

Potato starch was isolated in PPZ Trzemeszno Potato Enterprise, Poland. Sodium iodate(VII), potassium iodide, sodium thiosulfate and sodium carbonate, all of analytical grade, were purchased from POCH, Gliwice, Poland. D-(+)-Glucose was purchased from Sigma–Aldrich, Poland.

Glucoamylase OPTIDEX® L-400 401-04122-001 (Genencor International, USA) isolated from fungus, had activity 365 U/g at pH 4.0–5.5 at 35–40 °C. One unit of activity is defined as the amount of enzyme liberating 1 g of reducing sugars calculated as glucose from a soluble starch per hour under the specified conditions of the assay.

2.2. Methods

2.2.1. Starch illumination

Aqueous suspensions of potato starch (0.24 g starch/1 mL water) were illuminated with LPVL (Fiedorowicz & Rębilas, 2002; Fiedorowicz, Tomasik, & Lii, 2001) for 24 h from the 30 cm distance with a KB 502 slit illuminator (Kabid, Chorzów, Poland) equipped with 150 W xenon arc (XBO 150, Oriel, Maidston, UK). An HN 22 linear polarizing filter (Polaroid, Waltham MA, USA) with glass filter cutting out wavelengths below 500 nm was mounted

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between slit illuminator and the sample. The light source emitted continuous radiation in the visible range. Its energy flux at the position of the sample was 2.3 mW/g starch as checked by YSI radiometer (Yellow Spring, USA). Non-illuminated starch soaked in water for 24 h prior to the oxidation served as control. Samples of starch were illuminated and stored at 20 ± 1 °C.

2.2.2. Preparation of dialdehyde starch (DAS)

DAS was prepared from potato starch and sodium iodate(VII) with electrochemical recovery of the oxidant according to Para et al. (2000). The reaction vessel made of a lead plate served as anode and a stainless steel block cooled with water functioned as the cathode. The reaction vessel was filled with aqueous suspension (500 mL) of starch (30 g) and sodium iodate(V) (10 g), while the cathode cell, separated from the reaction vessel with a ceramic membrane, was filled with diluted (3% w/w) sulphuric acid. Electrolysis was conducted at 30 °C for either 30 min or 1 h with the 4A current. pH 5 of starch suspension was maintained during

Table 1
Change of aqueous solubility and degree of solubility (DO) of native starch after illumination with LPVL.

Starch sample	DO [%]	Solubility [%]
Native		
Non-illuminated	<0.5	<0.5
Illuminated	<0.5	<0.5
Non-illuminated oxidized for		
30 min	9.3	0.9
60 min	19.3	2.4
Illuminated oxidized for		
30 min	10.4	12.0
60 min	28.4	14.2

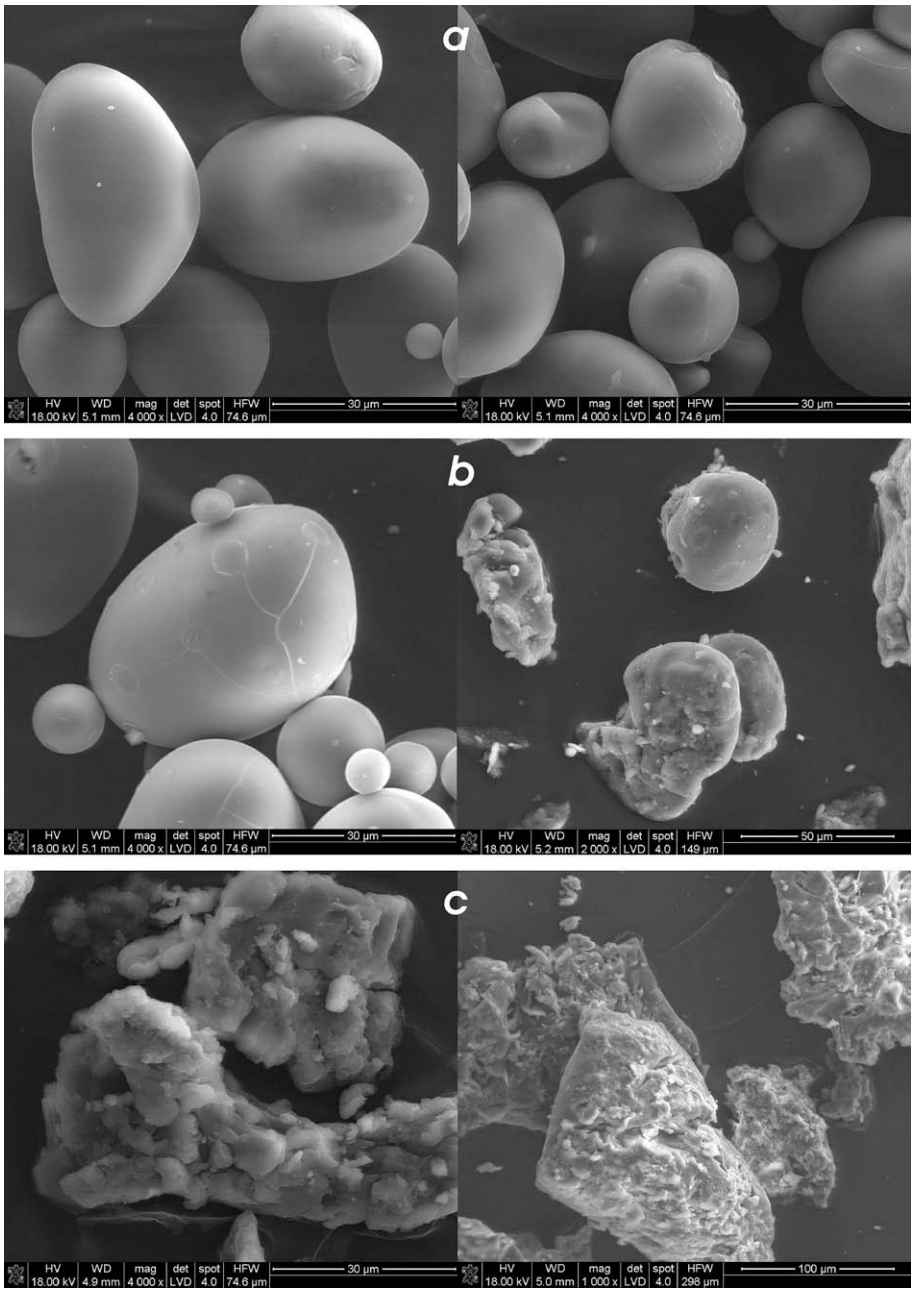

Fig. 1. SEM micrograph of: (a) native, non-illuminated (left) and illuminated (right) starch, (b) non-illuminated (left) and illuminated (right) starch oxidized for 30 min, (c) non-illuminated (left) and illuminated (right) starch oxidized for 60 min.

the reaction by admixing small doses of solid sodium bicarbonate when necessary (~4 g).

After electrolysis, starch was filtered off and washed with water (3 × 50 mL). The deposit collected on the filter was suspended in water (100 mL), and dry KI (0.01 g) followed by $Na_2S_2O_3$ (1 g) was added in order to remove residual iodate(V). Colorless product was filtered off, washed with small portions of water until filtrate was free of thiosulfate ions and dried at 50 °C.

Degree of oxidation (DO) of DAS was determined in duplicate with the oxime method (Krajcinovic, 1948; Veelaert, de Wit, & Tournois, 1994).

2.2.3. Characterization of dialdehyde starches

Solubility in water was estimated in duplicate according to Richter, Augustat, and Schierbaum (1968, chap. 9).

X-ray diffractograms were recorded using X'pert type Phillips diffractometer (Eindhoven, The Netherlands) with a cobalt lamp of λ = 1.7889 Å (30 mA and 40 kV) and in the scanning region of 2θ from 5° to 60° in 0.02° intervals.

E-SEM XL30 (FEI Company, Hillsboro, Oregon, USA) instrument with variable vacuum was used for scanning electron microscopy measurements. Starch samples were suspended in acetone to obtain a 1% suspension. One drop of the starch–acetone suspension was applied on an aluminum stub using double-sided adhesive tape and the starch was coated with gold powder to avoid charging under the electron beam after the acetone volatilized. An accelerating potential of 30 kV was used during acquisition of micrographs.

2.2.4. Enzymatic hydrolysis

Starch was gelatinized for 20 min at 85–90 °C in acetate buffer pH 5.5 (starch concentration was 1 mg/mL). After cooling to 37 °C, enzyme (3.7 U/mg starch) was added on gentle stirring (30 rpm). Samples were then incubated at 37 °C for up to 140 min on mild agitation. The enzyme was deactivated with 3,5 dinitrosalicylic acid solution (0.5%) and the concentration of reducing sugars are determined according to Southgate (1991) using 2101PC, Shimadzu spectrophotometer set for λ = 530 nm. D-(+)-Glucose was the standard. Estimations were run in duplicate.

3. Results and discussion

As shown in Table 1 24 h illumination of starch with LPVL had no effect upon its solubility and DO but the oxidation of non-illuminated and illuminated starch produced DAS of different properties. Non-illuminated starch after the 30 and 60 min oxidation provided products of DO 9.3% and 19.3%, and aqueous solubility of 0.9% and 2.4%, respectively. Identical 30 and 60 min oxidation of LPVL illuminated starch provided DAS of DO 10.4% and 28.4% and aqueous solubility of 12.0% and 14.2%, respectively.

Changes in the surface image of granules could be observed with SEM. Granules of native starch were smooth and uniform. After illumination with LPVL, the granule surface become non-uniform and cracked (Fig. 1a).

Non-illuminated starch after 30 min oxidation retained its granularity, although granules were damaged to a considerable extent and after the 60 min oxidation the granularity almost completely ceased (Fig. 1b and c). Granules of illuminated starch faced more pronounced changes on the oxidation (Fig. 1b and c). Residual granularity could be recognized after the 30 min oxidation whereas after the 60 min process granularity completely vanished. Thus, illumination of granular starch promoted its reactivity and, hence, provided products of higher DO.

X-ray powder diffractograms showed that LPVL illumination of granular starch did not change their crystallinity (Fig. 2a). Oxidation of non-illuminated starch for 30 min produced unessential

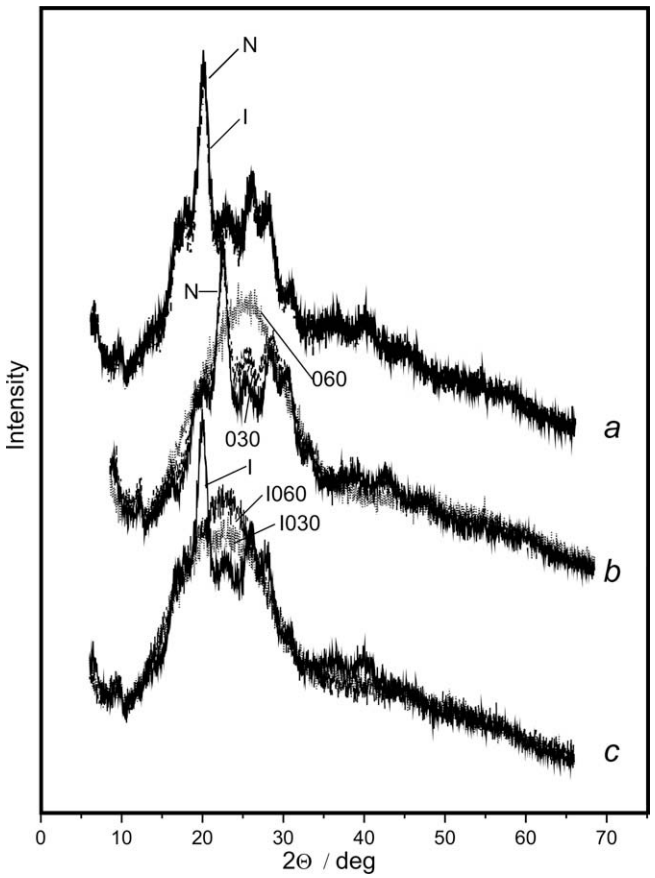

Fig. 2. X-ray powder diffraction patterns of: (a) native non-illuminated (N) and illuminated (I) starch, (b) native non-illuminated (N), non-illuminated and oxidized 30 min (O30) and 60 min (O60), (c) illuminated (I), illuminated and oxidized 30 min (IO30) and 60 min (IO60).

changes in its crystallinity but after the 60 min oxidation it turned fully amorphous (Fig. 2b). Illuminated starch lost its crystallinity already after 30 min oxidation (Fig. 2c) and which supported the earlier supposition about the role of LPVL in loosening granule structure.

Apparently, illumination could loosen the structure of starch granules facilitating penetration of the oxidant to the granule interior. An additional factor is that illumination caused depolymerization–repolymerization of amylopectin into amylose-like polysac-

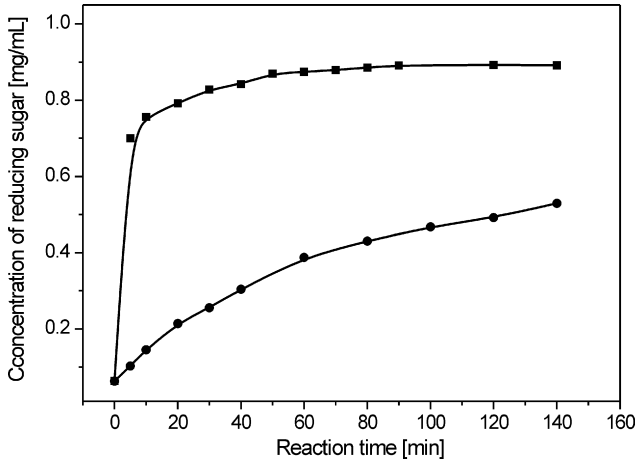

Fig. 3. The course of enzymatic hydrolysis of non-illuminated (–●–) and illuminated (–■–) starch.

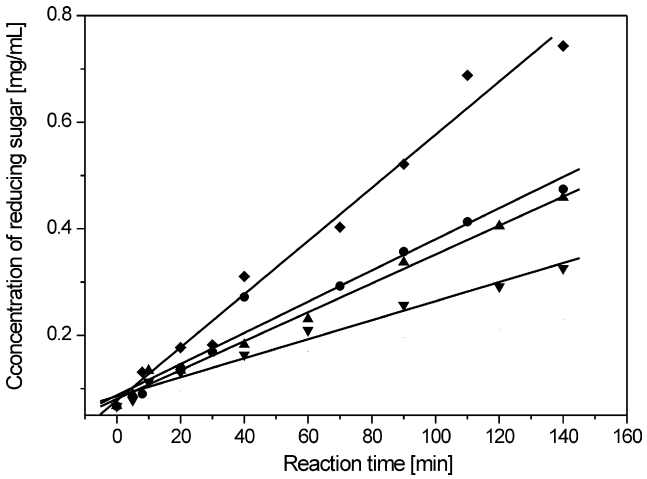

Fig. 4. Course of the enzymatic hydrolysis of oxidized for 30 min (–●–) and 60 min (–▲–), illuminated and oxidized for 30 min (–♦–) and 60 min (–▼–) starch.

Table 2
Rate constants for the enzymatic hydrolysis of non-illuminated and illuminated oxidized starches.

Starch sample	Rate constant $k \times 10^{-3}$ [mg ml^{-1} min^{-1}]
Non-illuminated oxidized for	
30 min	3.0 ± 0.1
60 min	2.7 ± 0.1
Illuminated oxidized for	
30 min	5.2 ± 0.3
60 min	1.8 ± 0.1

charide (Fiedorowicz et al., 2001) which could also be a factor responsible for observed results.

There was a powerful effect of LPVL upon enzymatic hydrolysis of potato starch (Fig. 3).

Concentration of reducing sugars formed from illuminated starch within few minutes of the process reached the same level as that from non-illuminated starch within 2 h. Progress in formation of reducing sugars during the hydrolysis of non-illuminated starch was observed just after 60 min of enzymatic digestion. The enzymatic hydrolysis of non-illuminated starch was completed within 140 min while the illuminated starch required only 40 min to reach the same level of the sugars.

The oxidation of illuminated starch decreased the susceptibility of the preparation to the enzymatic digestion and that decrease became more pronounced with the oxidation time, that is with increasing amount of the aldehyde group.

The susceptibility of 30 min oxidized illuminated starch exceeded that of 30 min oxidized non-illuminated starch (Fig. 4). Also 60 min oxidized non-illuminated starch was more susceptible to the enzymatic hydrolysis (Fig. 4). Table 2 shows rates of hydrolysis for particular cases. Reaction rate decreased with the oxidation time. The 30 min oxidation had almost negligible effect upon the reaction rate whereas the 60 min oxidation revealed clear differences in the rates of the process.

Likely, these differences resulted not only from DO of starch but also from the degree of depolymerization–repolymerization of starch which assisted the oxidation (Para et al., 2000).

4. Conclusions

1. Illumination of potato starch with linearly polarized visible light damaged the starch granule, increasing the susceptibility of the granules to the enzymatic hydrolysis without changes of the crystallinity in the granule interior.
2. Illumination with linearly polarized visible light increases susceptibility of the granules to the periodate oxidation.
3. Under identical oxidation conditions illuminated starch provides starch dialdehyde of slightly higher degree of oxidation and considerably higher aqueous solubility.

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