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Structural and molecular properties of dialdehyde starch

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Abstract

Dialdehyde starch (DAS) of degree of oxidation (DO) of 1.5% (DAS1-5), 5% (DAS5), 15% (DAS15) and 25% (DAS25) was prepared from potato starch in the periodate oxidation reaction with electrochemical recovery of the oxidant. Molecular weights (M_w) and radii of gyration (R_g) of polysaccharide chains of native and oxidized starches were measured by means of a high-performance size exclusion chromatography coupled with multiangle laser light scattering and refractive index detectors. The weight average molecular weight (M_w) and radius of gyration (R_g), calculated for the whole complicated peak of the eluate of native starch were 30.0×10^6 and 119.6 nm, respectively. The oxidation induced instant degradation of starch polysaccharide chains.

M_w value of the chains of the polysaccharide molecules eluted from the sample of DO 1.5% (DAS1-5, 2.2×10^6) was by one order lower than the average molecular weight of native starch molecules (30×10^6). Even more significant decrease in molecular weight up to 6.4×10^4 was observed for the DAS5 sample. The chain length distribution of amylopectin structural units of native and DAS was characterized by the hydrolysis with isoamylase followed by treatment with β-amylase. Chain distribution profiles of completely debranched samples were available from a high-pressure size exclusion chromatography with multiangle laser light scattering and refractometric index detectors. The oxidation slightly changed the average molecular weight (M_w) of the A-type chains although it evoked changes in the mass ratio of the A-type chains. The weight average molecular weight M_w and mass ratio of B-type chains significantly differed depending on DO of the sample. X-ray diffraction patterns indicated that crystallinity of DAS1-5 and DAS5 decreased in relation to native starch. Oxidised starches of the highest DO were fully amorphous.

Keywords: Dialdehyde starch; Size exclusion chromatography; Molecular weight

1. Introduction

Dialdehyde starch (DAS) from the periodate oxidative cleavage of the C(2)–C(3) bond of the anhydroglucose units of starch polysaccharide chains found several industrial applications. Since aldehyde groups form hemiacetals and acetals, dialdehydes, such as glyoxal and glutaraldehyde, has been successfully used in cross-linking acetalation of cellulose derivatives (Maurer, 1969). Industrial applications of dialdehyde starch are also based on its cross-linking ability. Majority of DAS production is consumed by the paper industry as wet-strength improver (Jetten, Timmmerman, Besemer, Van den Dool, & Boumans, 2003; Schneider and Riella, 1980; Thornton, Van Brussel-Verraest, Besemer, & Sandberg, 2001).

Any use of dialdehyde starch as a component of foodstuffs is illegal because DAS induces cross-linking polypeptide chains and globulins (Schwenke, Prahl, Jamratz, Ender, Uhlig and Volnova, 1976). Nevertheless, DAS still evokes considerable interest of food industry because of its potential applications especially as component of biodegradable plastics for packaging purposes, superabsorbent and trap for removing of heavy metals from industrial waste (Tomasik and Schilling, 2004). Recently, it was shown that dialdehyde starch dithiosemicarbazone (Para and Ropek, 2000), disemicarbazone (Ropek and Para, 2002) and dihydrazone (Para, Karolczyk-Kostuch, & Fiedorowicz, 2004) form stable complexes with heavy metals and, therefore, it could be used for example as biodegradable trap for heavy metal ions from sewage and soil.

On the periodate oxidation, starch polysaccharide chains underwent fragmentation resulting in changes in the organisation of crystalline lamellae of starch granule and, in consequence, altering starch thermal and pasting properties, swelling power, solubility, and susceptibility to enzymatic hydrolysis. The model of starch granule (Gallant, Bouchet, & Baldwin, 1997) presents granule crystallites consisting of

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ordered double helical amylopectin side chain clusters, whereas amorphous parts contains linear, non-branched amylose chains. No data on differences in the susceptibility to degradation of polysaccharide chains from the amylose and amylopectin fractions from the periodate oxidation are available. Similarly, nothing is known about the oxidation induced changes in the chain length of amylopectin. This paper presents results of examination of the effect of periodate oxidation on X-ray diffraction patterns of starch granule, molecular weight of starch polysaccharide molecules, distribution of chain length of amylopectin side chains and iodine binding properties of starch polysaccharides.

2. Experimental part

2.1. Preparation of dialdehyde starch

Dialdehyde starch (DAS) was prepared from potato starch in the periodate oxidation reaction with electrochemical recovery of oxidant. Reaction vessel was made of lead plate and served as anode. Cathode was constructed from stainless steel. In the typical experiment, reaction vessel was filled with water suspension (700 cm^3) of starch (100 g) and sodium periodate(V) (20 g), while cathode compartment, divided from reaction vessel by ceramic barrier, was filled with diluted (3%, w/w) sulphuric acid. Electrolysis was conducted for 2–5 h with current in the range 1–8 A. Temperature of the reaction mixture was kept at 30 °C. Acidity of starch suspension during reaction course was maintained at pH = 5 level, by addition of small amounts of sodium bicarbonate (0.5 g).

After termination of electrolysis starch was filtered off and washed three times with water (50 cm^3). Starch again was suspended in water than dry KI followed by $Na_2S_2O_3$ was added in order to remove residual periodate(V). Colourless product was filtered off, washed with small portions of water until eluate was free of thiosulphuric ions and dried at 50 °C.

2.2. HPSEC-MALLS-RI

High-performance size exclusion column chromatography (HPSEC) system consisted of a pump (Shimadzu 10AC, Tokyo, Japan), an injection valve (model 7021, Rheodyne, Palo Alto, USA), a guard column (TSK PWH, Tosoh Corporation, Tokyo, Japan), and two connected together SEC columns TSKgel GMPWXL (7.8×300 mm, Tosoh Corporation, Tokyo, Japan) and TSK Gel 2000 PW (7.8×300 mm, Tosoh Corporation, Tokyo, Japan). A multiangle laser light scattering detector Dawn-DSP-F (Wyatt Technology, Santa Barbara CA, USA), equipped with He–Ne laser emitting light with wavelength 630.0 nm and a differential refractive index detector (L-7490, Merck, Darmstad, Germany) were connected to the columns. Columns were maintained at 50 °C and RI detector at 35 °C. The mobile phase (0.15 M $NaNO_3$ with 0.02% sodium azide) was filtered subsequently through 0.2 and 0.1 μm cellulose acetate filters (Whatman, England). Flow rate of mobile phase was 0.4 $cm^3\ min^{-1}$. The output voltage of refractive index (RI) and light scattering (LS) at 18 angles was used for calculation of the weight-average molecular weight (M_w) and radius of gyration (R_g) using Astra 4.73.04 software (Wyatt Technology, Santa Barbara CA, USA). Berry plot with third order polynomial fit was applied for the calculation of M_w and R_g values (Aberle, Burchard, Vorwerg, & Radosta, 1994; Bello-Perez, Paredes-Lopez, Roger, & Colonna, 1996; Hanselmann, Ehrat, & Widmer, 1995).

2.2.1. Calibration of detector

Calibration constant for the RI detector was determined by injection of five (0.05–0.50 $mg\ cm^{-3}$) aqueous NaCl solutions of known concentration into the detector. Output voltage from the detector was collected by Rical 2 software (Wyatt Technology, Santa Barbara CA, USA) and calibration constant was calculated from the slope of the $fn = c(dn/dc)$ vs voltage graph. The following values of dn/dc (change in refractive index with concentration) were used in calculation of the average molecular weight (M_w) and radii of gyration (R_g): pullulan 0.148, dextran 0.142, and starch 0.146. LS calibration constant for the diode at 90° was available from the LS intensity of toluene. Normalization of the response of the photodiodes arranged around the scattering cell to the diode at 90° was carried out using BSA. One pullulan and two dextran standards were applied for the accuracy test of the calibration.

The recovery of injected standards exceeded 95%. Determined M_w were 9.9×10^5, 6.2×10^5, 2.0×10^6 for for pullulan P-100, dextrans D-580, and D-2000, respectively. These estimations were in good match with those given by the manufacturer (9.8×10^5, 5.8×10^5, and 2.0×10^6, respectively).

2.2.2. Sample preparation for HPSEC

Native potato starch and oxidized starches of degree of oxidation 1.5% (DAS1-5) and 5% (DAS5) (1 g) moistened with water (10 cm^3) were suspended in dimethylsulfoxide (DMSO, 90 cm^3) then boiled for 2 h on agitation. Then the starch solution was agitated for 24 h at 25 °C, followed by precipitation of starch with ethanol (500 cm^3). The precipitate was centrifuged (2500 rpm, 20 min), washed three times with ethanol, and dried overnight under vacuum at room temperature. The purified starch (~5 mg) was wetted with ethanol (0.200 cm^3) and dissolved in 2 M NaOH (1 cm^3) by stirring for 1 h at 70 °C. An aliquot of 0.15 M $NaNO_3$ (17 cm^3) was then added. The starch solution, after neutralisation with 2 M HCl (1 cm^3) was diluted with 0.15 M $NaNO_3$ to obtain a final concentration of about 0.24 $mg\ cm^{-3}$.

Dialdehyde starches with degree of oxidation of 15% (DAS15) and 25% (DAS25) were dissolved directly in mobile phase at the same concentration. Prior to HPSEC injection, the solution was filtered through a 0.8 μm cellulose acetate filter. Injection volume was 0.500 cm^3.

2.3. Debranching

Starch sample (20 mg) was suspended in water (6.5 cm^3) and heated for 30 min (95 °C). After cooling starch solution was diluted with water (2.5 cm^3) and acetate buffer (pH = 3.5, 1 cm^3). Aliquots of stock solution of *Pseudomonas* *amyloderamosa* isoamylase (glycogen 6-glucanohydrolase EC.3.2.1.68) in acetate buffer (0.100 cm^3, 54,000 U/cm^3) was added and solution was incubated for 24 h at room temperature.

For a portion of the digest (2 cm^3), the pH was increased to 4.8 with acetate buffer (0.5 cm^3, pH = 4.8) followed by addition of β-amylase (20 mg, 29 U/mg). Incubation was completed after 24 h by bringing the samples to boiling.

2.4. Unit chain distribution

High-performance size exclusion chromatography was performed using HPSEC-MALLS-RI system. Flow rate of the solvent (0.15 M $NaNO_3$) was 0.40 cm^3 min^{-1} and injected sample volume was 0.100 cm^3.

2.5. X-ray diffractometry

X-ray powder diffractometry was performed according to Gerard, Colonna, Buleon, and Planchot (2001). Thus, samples of native and illuminated material were adjusted to 200 g kg^{-1} of the water content. Equilibrated samples were sealed between two tape foils to maintain a stable water content throughout the measurement. Diffraction diagrams were recorded using X'pert type Phillips diffractometer with a cobalt lamp of $\lambda =$ 1.78896 Å (30 mA and 40 kV) and in the scanning region of 2(from 5 to 60° in 0.02° intervals.

2.6. Iodine staining

The blue value and λ_{max} of samples of native and dialdehyde potato starch were determined by the Shimadzu 2101 PC UV–vis spectrophotometer (Shimadzu, Japan) according to Morrison and Lainglet (1983) with modifications described by Klucinec and Thompson (1998). Thus, starch (40 mg) was dispersed in 10 cm^3 of DMSO containing 10% 6 M urea. A 1.0 cm^3 aliquot of each sample was placed in a 100 cm^3 volumetric flask, to which 95 cm^3 of deionized water and 2 cm^3 of an aqueous I_2–KI solution was added. The latter solution was prepared of 200 mg of I_2 and 2 g of KI in 100 cm^3 of distilled water. The mixture was brought to 100 cm^3 with deionized water and mixed immediately. Blank solutions were prepared identically did not contain starch. Spectra in the range of 500–800 nm were measured for all samples using Shimadzu 2101 PC UV–vis spectrophotometer (Shimadzu, Japan). The blue value of samples was defined as the absorbance at 640 nm. The λ_{max} was the peak absorbance value over the range of wavelengths examined. All measurements were run in triplicates.

3. Results and discussion

3.1. X-ray analysis

Diffractograms of native and oxidised potato starches are presented in Fig. 1.

Diffractograms of native potato starch exhibited the typical B-type pattern (Tian, Rickard, & Blanshard, 1991). In diffractograms of DAS1-5 and DAS5 the reflection bands centered around 5.5 and 13–15 2θ were much lower and more diffuse than in the diffractogram of native potato starch. Diffractograms taken for samples DAS15 and DAS25 showed complete lack of reflections bands typical for amorphous samples. X-ray diffraction is widely used in studies of the starch granule organization (Hizukuri, 1996; Tian et al., 1991) carrying information on the regularly repeating nature of the double helical molecular structure.

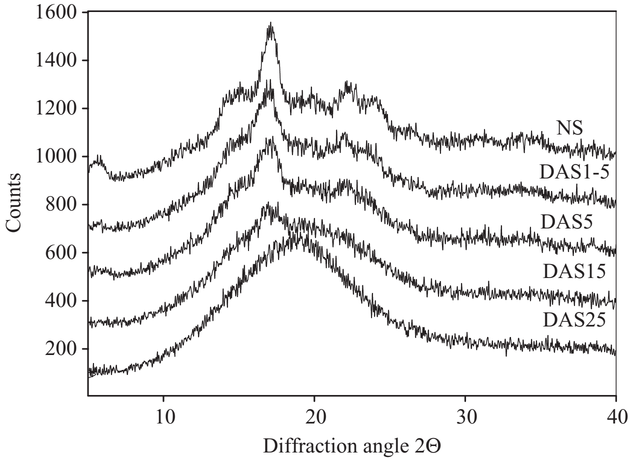

Fig. 1. X-ray diffraction patterns of native (NS) and dialdehyde potato starch of 1.5% (DAS1-5), 5% (DAS5), 15% (DAS15) and 25% (DAS25) degree of oxidation.

Thus, the differences observed in diffraction patterns of dialdehyde potato starch clearly indicated a gradual collapse of the crystallinity within samples with lowest degree of oxidation (DAS1-5 and DAS5) followed by total loss of crystallinity observed for samples with higher degree of oxidation (DAS15 and DAS25).

Potato starch, the tuber starch, has a high content of phosphorus relative to cereal starches (Lin and Czuchajowska, 1998; Zobel, 1998). This starch is the sole known variety with phosphate groups residing in the long chains of amylopectin (Hizukuri, Tabata, & Nikuni, 1970; Rooke, Lampitt, & Jackson, 1949). It was shown that crystallinity of potato starch granules depended on degree of phosphorylation (Blennow, Bay-Smidt, Wischmann, Olsen, & Moller, 1998). Thus, the phosphate moieties could contribute to the rigidity of the amylopectin chains and their macro-scale organisation making the matrix more rigid. This could explain that very significant drop in M_w of polysaccharide chains indicating their fragmentation, observed for dialdehyde starches even with low degree of oxidation (DAS1-5 and DAS5), did not lead to complete collapse of crystalline structure.

3.2. HPSEC-MALLS-RI

Superimposed chromatograms taken with LS and RI detectors for native potato starch together with RI chromatogram of DAS5 are presented on Fig. 2.

Due to big differences in retention times and shapes of peaks registered for native and oxidised starch samples, weight

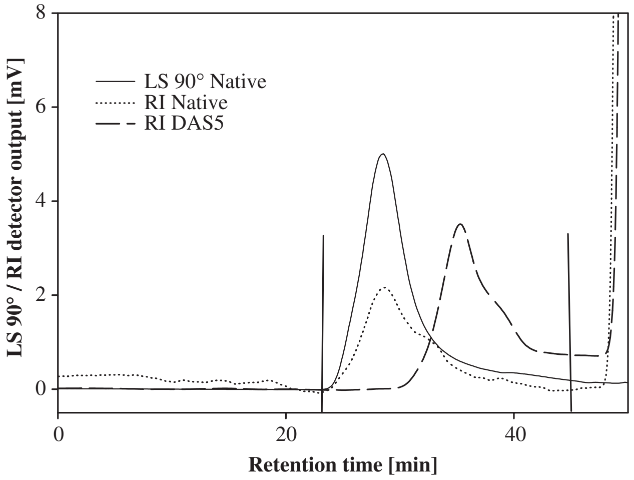

Fig. 2. Chromatograms of RI and LS 90° detector outputs for native potato starch and DAS5 sample, eluted from size exclusion columns.

average molecular weight M_w and radius of gyration R_g were calculated for the whole complicated peak of eluate of each sample. The M_w and R_g values for native and dialdehyde starch samples are given in Table 1.

Presented data clearly shown that oxidation initiated almost instant degradation of starch polysaccharide chains. M_w value of chains eluted from sample with lowest degree of oxidation DAS1-5 (2.2×10^6) was one order of magnitude lower than average molecular weight measured for native starch molecules (30×10^6). Even more significant drop of molecular weight up to 6.4×10^4 was observed for sample DAS5.

Samples of degree of oxidation 15 and 25% shown similar M_w values 6.8×10^3 (DAS15) and 5.1×10^3 (DAS25), respectively. Oxidation led to gradual decrease in R_g of dialdehyde starch molecules. However, changes in R_g did not correlate with changes in M_w observed for oxidised starches. Polysaccharide molecules from sample DAS1-5 shown M_w value one order of magnitude greater than those from sample DAS5, while their R_g values 48.2 nm (DAS1-5) and 32.5 nm (DAS5) did not differ significantly. On the other hand, small difference in molecular weight between samples DAS15 and DAS25 is accompanied by big difference in R_g values (17.0 and 3.4 nm, respectively).

Data from both RI and LS detectors provided calculations of differential molar mass distribution with the Astra 4.73.04 software. The differential molar mass distribution provided the amount of material (differential weight fraction) in a given molar mass interval. Differential molar mass distribution $x(M)$ was calculated with Eq. (1):

$$x(M) = \frac{\mathrm{d}W(M)}{\mathrm{d}(\log M)} = \frac{-h(V)}{f(V)} \tag{1}$$

where $h(V)$ was the normalised concentration at volume of V and $f(V) = \mathrm{d}(\log M)/\mathrm{d}V$ was the slope of the calibration curve determined by the light scattering measurements. The normalised concentrations $h(V)$ were given by Eq. (2)

$$h(V) = \frac{c_i}{\sum c_i \Delta V} \tag{2}$$

where c_i was the concentration at 0.500 cm^3 volume of eluate (slice) and ΔV was the volume per slice.

Table 1
Weight average molecular weights (M_w) and radii of gyration (R_g) of native and dialdehyde potato starch of 1.5% (DAS1-5), 5% (DAS5), 15% (DAS15) and 25% (DAS25) degree of oxidation

Sample	$M_w\times10^6$	R_g (nm)
Native	30.0±0.5	119.6±8.2
DAS1-5	2.20±0.2	48.2±1.0
DAS5	0.064±0.015	32.5±1.2
DAS15	0.0068±0.0005	17.0±0.9
DAS25	0.0051±0.0003	3.6±0.3

Plots of the differential molar distribution for native potato starch and oxidised starches DAS1-5, DAS5, DAS15 and DAS25 are given in Fig. 3.

Significant drop in M_w of polysaccharide chains observed for DAS1-5 did not lead to major changes in patterns of molecular weight distribution as compared with native starch. Additionally, it seems that this sample did not contain molecules with small molecular weigh. However, it could be seen that sample DAS5 contains molecules with broadest distribution of molecular weight, ranging from few thousands to several hundred thousands Daltons. One could assume that during first stage of oxidation only [1–4] glycosidic bonds between anhydroglucose moieties of amylose and amylopectin chains were broken, leading to formation of molecules with comparably compact distribution of molecular weight. Further oxidation led to disruption both [1–4] and [1–6] glycosidic bonds which results in formation of chains differing greatly in M_w as it was observed for sample DAS5. Samples with highest degree of oxidation, i.e. DAS15 and DAS25 contained almost completely degraded polysaccharide chains. It is worthy to note that molecules with M_w value $<10{,}000$ constituted vast majority of sample DAS25.

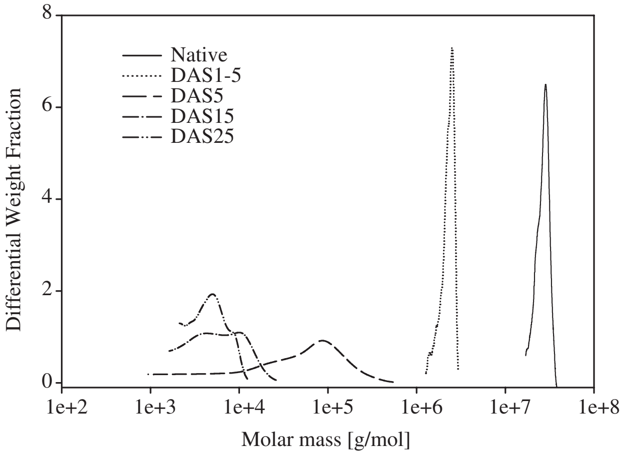

Fig. 3. Plots of differential weight fraction versus molar mass for native potato starch (native) and dialdehyde starch of 1.5% (DAS1-5), 5% (DAS5), 15% (DAS15) and 25% (DAS25) degree of oxidation.

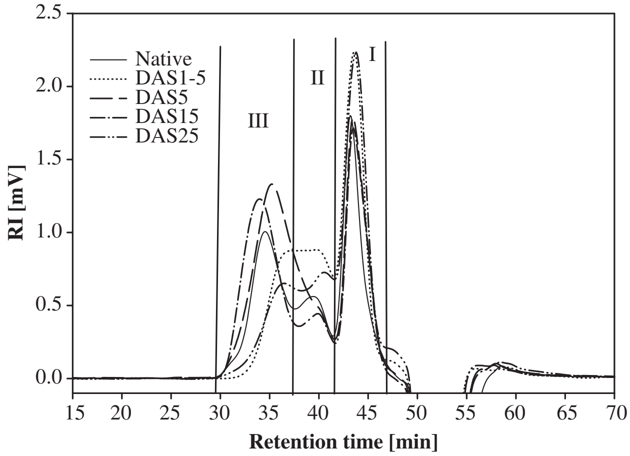

Fig. 4. Superimposed chromatograms of RI detector output for isoamylase debranched samples of native potato starch eluted from size exclusion column. The DAS1-5, DAS5, DAS15, and DAS25 notation relates to samples of dialdehyde starch of 1.5, 5, 15 and 25% degree of oxidation respectively. Regions I, II, III were established for A-type, B-type, and amylase type chains fractions, respectively.

3.3. Distribution of amylopectin structural units

Chromatograms of the isoamylase debranched samples of native and dialdehyde potato starch samples are presented in Fig. 4.

The RI curve for native starch was separated into two portions corresponding to the A-(I) and B-(II) type amylopectin side chains, together with a peak attributed to the amylose-type long carbohydrate chains (III). Average molecular weight and mass ratio of eluted molecules belonging to each peak were calculated (Table 2).

It is widely accepted that the amylopectin component of all starches is built up of short clustered chains (Gallant et al., 1997; Hizukuri, 1984; 1986). Amylopectin side chains are grouped into two major categories (Hizukuri, 1984). A-type chains are defined as non-branched chains. Short B-type chains (B_1 chains) are branched with other (A- and/or B-type) chains. The amylopectin clusters are interconnected by longer B-type chains that are denoted as B_2–B_4 chains and span 2–4 clusters, respectively. According to Hizukuri (1984), low-molecular weight chains eluted in fraction (I), could be attributed to the amylopectin side chains of the A-type. Fraction (II) contained a mixture of the B_1-type and longer $B_{\geqq 2}$-type amylopectin side chains.

Chromatogram patterns of debranched dialdehyde starch samples DAS1-5, DAS5, DAS15 and DAS25 differed significantly from chromatogram of native starch. For each oxidized starch sample average molecular weight and mass ratio of molecules eluted in each of the regions set for native starch was calculated (Table 2).

Taking into account shape of chromatograms observed for oxidized starches it seems obvious that oxidation of amylopectin chains led to changes in polysaccharide structure, probably in near vicinity of branching point, which in consequence at least diminished ability of enzyme to hydrolyse [1–6] glycosidic bonds. Simultaneously, small polysaccharide molecules resulted from scission of glycosidic bonds induced by oxidation reaction could elute in the regions set for native potato starch. Therefore, obtained results should be regarded as apparent distribution of molecules in isoamylase hydrolized dialdehyde starch samples.

It seems that oxidation reaction lightly changed average molecular weight of the A-type chains although it evoked changes in mass ratio of the A-type chains. In the native sample, such chains constituted 38% of the total mass. This contribution rose gradually of degree of oxidation to 43.8% (DAS1-5), 59.3% (DAS5) and 62.3% (DAS15). However, in sample with highest degree of oxidation (DAS25) chains eluted in region I constituted only 38.8% of total mass and exhibited lowest M_w (0.9×10^3).

M_w and mass ratio of polysaccharides eluted in region II differ greatly depended on sample degree of oxidation. In sample DAS1-5 with lowest degree of oxidation and therefore resembling native starch, molecular weight of chains eluted in region II (B-type) drop to 3.62×10^3, while their mass ratio rose to 39.9% as compared to native (13.5×10^3 and 23%, respectively) probably due to elution of molecules resulted from amylose and/or amylopectin degradation. Samples of degree of oxidation 5 and 15% contained molecules eluted in region II with much higher molecular weight (8.17×10^3 and 11.8×10^3) and smaller mass ratio (6.60 and 16.7%) than sample DAS1-5.

Among chains eluted in region III molecules from sample DAS1-5 exhibited lowest molecular weight (11.28×10^3). It is worthy to note that dialdehyde starches of high degree of oxidation, i.e. DAS5, DAS15, DAS25 showed much higher M_w values (28.6×10^3, 55.0×10^3 and 46.7×10^3, respectively) for molecules eluted in region III than DAS1-5.

3.4. Iodine binding properties

Iodine binding properties for illuminated and non-illuminated waxy corn starch and corn amylopectin samples are presented in Table 3.

Table 2
Weight average molecular weights M_w and relative mass m (%) of the amylopectin structural units of native and dialdehyde potato starch of 1.5% (DAS1-5), 5% (DAS5), 15% (DAS15) and 25% (DAS25) degree of oxidation

Sample	Peak I A-type chains		Peak II B-type chains		Peak III Amylose type chains	
	$M_w\times10^3$	m (%)	$M_w\times10^3$	m (%)	$M_w\times10^3$	m (%)
Native	3.44±0.5	38.0	13.5±0.6	23.0	68.0±1.0	38.0
DAS1-5	1.16±0.3	43.8	3.62±0.5	39.9	11.28±0.6	16.3
DAS5	3.34±0.4	59.4	8.17±0.6	6.60	28.62±0.6	34.0
DAS15	2.42±0.4	62.3	11.8±0.5	16.7	55.0±0.7	21.0
DAS25	0.91±0.3	38.8	4.22±0.4	27.1	46.68±0.8	34.1

Table 3
UV spectral data of the starch–iodine complexes of native (NS) and dialdehyde starch of 1.5% (DAS1-5), 5% (DAS5), 15% (DAS15) and 25% (DAS25) degree of oxidation

Sample	λ_{max} (nm)[a]	E_{max}[b]	E_{640} BV[c]	E_{525}[d]	E_{640}/E_{525}
NS	599.0	0.323	0.292	0.213	1.37
DAS1-5	590.0	0.362	0.315	0.256	1.23
DAS5	517.5	0.158	0.059	0.155	0.38
DAS15	480.5	0.023	0.005	0.017	0.29
DAS25	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Absorbance at maximum.
[b] Absorbance maximum.
[c] Absorbance at 640 nm (blue value, BV).
[d] Absorbance at 525 nm.

It was shown that the λ_{max} of starch iodine complexes depends on the length of the glucan helices (Banks, Greenwood, & Khan, 1971; Handa, Yaijima, Ishi, & Nishimura, 1981) and λ_{max} asymptotically approaches 640 nm for degree of polymerisation >200. Therefore, the E_{640}/E_{525} ratio, where E is extinction measured at 640 and 525 nm, respectively, could be regarded as a measure of the ratio of short chain branched (scb) and amylose-type non-branched/long-chain branched (nb/lcb) glucans.

Values of iodine binding capacity, expressed as E_{640}/E_{525} ratio, exceeding 1.5 are clear indication for amylose type, nb/lcb, starch glucans (Bailey and Wehen, 1961; Pfanemuller, Mayerhofer, & Schulz, 1971). Praznik, Mudlinger, Kogler, Pelzl, and Huber (1999) showed that the ratio of short chain branched (scb) and amylose-type non-branched/long-chain branched (nb/lcb) glucans correlate with rheological properties, freeze/thaw performance, and water binding properties of starches of different botanical origin.

In the case of DAS1-5 significant rise of blue value (0.315) and E_{max} (0.362) as compared to native starch (0.292 and 0.323, respectively) was observed. Such effect could be attributed to formation, during oxidation reaction, of additional non-branched polysaccharide chains due to debranching of longest amylopectin side chains. Weight average molecular weight M_w of polysaccharide chains measured for the whole eluted peak of this sample, found to be lower of one order magnitude than M_w for native starch, indicate that molecules with M_w typical for amylose type chains constitute vast majority of DAS1-5. Similarly drop in hydrodynamic radius value R_g observed for DAS1-5 (48.2 nm) as compared with native starch (48.2), support assumption of formation of non-branched glucans in this sample. However, one could not exclude possibility that iodine complex of even slightly oxidized starch helices will have different extinction coefficient than iodine complex of native chains.

Samples of starch with higher degree of oxidation, i.e. DAS5 and DAS15 exhibited gradual decrease of all measured iodine binding properties. Dialdehyde starch with 25% degree of oxidation (DAS25) apparently did not form any iodine complex. Those results indicate gradual fragmentation of polysaccharide molecules during starch oxidation and are in full accordance with M_w and R_g values measured by size exclusion chromatography.

4. Conclusions

Periodate oxidation of potato starch leading to formation of dialdehyde starch induced disruption of starch polysaccharide chains. M_w and R_g of molecules formed during oxidation greatly depended on the degree of oxidation diminishing for DAS of lowest degree of oxidation (DAS1-5) one order of magnitude as compared with native starch. Dialdehyde starches with highest degree of oxidation (DAS15 and DAS25) contained chains with average molecular weight below 1×10^4. However, disruption of polysaccharide chains led to complete lack of crystallinity indicating dissipation of starch granules, only for dialdehyde starch of highest degree of oxidation (DAS25).

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