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Physicochemical properties of waxy corn starch and corn amylopectin illuminated with linearly polarised visible light

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Abstract

Aqueous suspensions (30%) of either waxy corn starch or corn amylopectin were illuminated with visible linearly polarised light ($\lambda > 500$ nm) for 5–50 h. Pasting profiles, thermal properties, iodine binding capacity and intrinsic viscosity (in DMSO/water, 90:10) were taken for them after illumination. The illumination for 5, 15, and 25 h was not reflected in overall paste viscosities. Prolonged illumination (50 h) led to significant decrease in the peak and final viscosities. Illumination for 5 h (6.76 J/g), 15 h (7.74 J/g), 25 h. (7.95 J/g), and 50 h (2.85 J/g) decreased the melting enthalpies which for original waxy corn starch was 9.67 J/g. Decrease in intrinsic viscosity, $[\eta]$, as compared to that of native waxy corn starch (7.9 dl/g) was observed for the sample illuminated for 15 h (5.9 dl/g). Further illumination led to increase in $[\eta]$ values after 25 h (6.6 dl/g) and 50 h (8.0 dl/g). Blue value (BV) measured for the sample illuminated for 5 h (0.106) was higher than for waxy corn starch (0.076). Gradual decrease in BV was observed for samples illuminated for 15 (0.086), 25 (0.071) and 50 h (0.030). No changes in intrinsic viscosity and BV were found in the case of corn amylopectin irrespective of the illumination time. Findings indicate that polarised light induced depolymerisation of starch polysaccharide only if molecules were organised in crystal structures in same manner as in starch granule.

Keywords: Aqueous suspensions; Illumination; Viscosities

1. Introduction

Degradation of starch after illumination with the moonlight was previously reported (Navez & Rubenstein, 1928; Semmens, 1947). Navez and Rubenstein (1948) attributed degrading action of polarised light on starch to enzymatic action. However, Semmens (1947) found that moonlight directly hydrolysed starch polysaccharides. In our previous work (Fiedorowicz, Tomasik, & Lii, 2001) results of illumination of normal corn starch with visible polarised light for a short time (5–15 h) were described. It induced formation of low molecular weight polysaccharide molecules and sharp decrease in the molecular weight of amylopectin and, to lesser extent, amylose fractions of illuminated starch. Prolonged illumination (25–50 h) resulted in cross-linking of small polysaccharide molecules and polysaccharide chains belonging to amylopectin fraction of starch. The same effect was observed for starch preheated at 120 °C before illumination suggesting non-enzymatic mechanism of polarised light action on starch. Similar effect, i.e. degradation of polysaccharide molecules followed by recombination reaction was described for normal corn starch irradiated in the air with UV light (Fiedorowicz, Tomasik, You, & Lim, 1999).

Absorbtion of UV light by acetal chromophore at C-1 position of the D-glucose moiety followed by subsequent photoreactions (Merlin & Fouassier, 1981; Phillips & Rickards, 1969) led to the formation of highly reactive peroxide. It explained the mechanism of observed cross-linking.

However, polysaccharide molecules constituting starch granule did not absorb visible light. Therefore, action of visible polarised light cannot be explained by the mechanism proposed for UV induced starch reactions. On the other hand, it is known that light with its electrical vector parallel to longer axis of double helical polysaccharide chains is strongly absorbed (Rundle & Baldwin, 1943; Rundle & French, 1943).

According to recent model proposed by Gallant, Bouchet, and Baldwin (1997) crystalline parts of starch granule consists of ordered double helical amylopectin side chain clusters, capable of absorbing polarised light. Therefore, we decided to examine the effect of visible polarised light on waxy corn starch containing organised crystalline structures and amorphous isolated corn amylopectin.

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2. Materials and methods

2.1. Materials

Waxy corn starch was generously provided by National Starch and Chemicals (Neustadt, Germany). Corn amylopectin and DMSO was purchased from Sigma Chemical Co. (St. Louis, MO, USA).

2.2. Illumination

Aqueous 30% waxy corn starch and corn amylopectin slurry were illuminated from 30 cm distance with the KB 502 slit illuminator (Kabid, Chorzow, Poland) equipped with 150 W xenon arc lamp XBO 150 (Oriel, England). The HN 22 linear polarising filter (Polaroid, USA), with glass filter cutting off wavelengths below 500 nm was mounted between the slit illuminator and the sample. Illumination at 25 °C on agitation was carried out under nitrogen (5 ml/min) for 5, 15, 25, and 50 h. Illuminated starch or amylopectin was filtered (Whatman 41, England) under reduced pressure than dried at 50 °C for 24 h.

Samples of starch and amylopectin, kept in dark under the same conditions as illuminated samples, served as control. The physicochemical characteristics of those samples were similar to that of native starch or amylopectin. Therefore, only those samples of starch and amylopectin (WPLN-50 and APLN-50) kept in dark for 50 h are presented for comparison.

The light source emitted continuous intensity in the visible range. Its energy flux at the place of the samples was 8 mW/cm^2 as checked by YSI radiometer (Yellow Springs, USA).

2.3. Thermal properties

Thermal properties of illuminated waxy corn starch and control were determined by means of a differential scanning calorimeter Setaram DSC 121 (Setaram Co. France). The starch (1.5–2.0 mg) was sealed in an aluminium pan with water at 1:4 starch/water w/w ratio. Samples were heated from 25 to 125 °C at the rate of 10 °C/min. Empty pan was used as reference.

2.4. Pasting properties

Pasting curves of native and illuminated waxy corn starch (8% w/w) were measured with Rapid Viscoanalyzer (RVA, Newport Scientific, Newport, Australia). The starch suspensions were kept at 35 °C for 1.10 min, then heated to 95 °C at the rate of 6.0 °C/min, maintained at this temperature for 4 min, cooled to 35 °C at the rate 6 °C/min, and kept at 35 °C for 5 min.

2.5. Iodine staining

The blue value (BV) and λ_{max} of illuminated samples of waxy corn starch and corn amylopectin 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 ml of DMSO containing 10% of 6 M urea. A 1.0 ml aliquot of each sample was placed in a 100 ml volumetric flask, to which 95 ml of deionised water and 2 ml of an aqueous I_2–KI solution was added. The latter solution was prepared with 200 mg of I_2 and 2 g of KI in 100 ml of distilled water. The mixture was made up to 100 ml with de-ionised water and mixed immediately. Blank solutions that 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 BV 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.

2.6. Intrinsic viscosity

Solutions for rheological measurements were prepared by the addition of 100 mg of appropriate waxy corn starch or amylopectin into 100 ml volumetric flask containing 10 ml of distilled water and gently agitated with magnetic stirrer at 30 rpm to moisturise and disperse the granules thoroughly. The stirring continued and 60 ml of DMSO was added. The flask was then heated gradually for 20–30 min to 80 °C and kept for 3 h at this temperature. The solution was then cooled to 25 °C and additional DMSO was added to bring the total final volume to 100 ml. This stock solution was then diluted with DMSO and water (90:10) to desired concentrations.

Rheological properties of each solution were recognised using modified Zimm rotary viscometer. The temperature of the sample was maintained at 25 °C with an accuracy of 0.1 °C. For each sample seven different solutions in the concentration range from 0.0 to 0.1 g/dm^3 were measured. Intrinsic viscosities were obtained by the usual method of plotting reduced viscosity versus concentration. Data were extrapolated to zero concentration by linear regression.

3. Results and discussion

3.1. Thermal properties

Onset (T_0), peak (T_p), and conclusion (T_c) and transition enthalpy (ΔH) for the melting of native and visible polarised light illuminated starches are listed in Table 1. No significant changes in gelatinisation temperatures were observed for samples illuminated for 5, 15, and 25 h when compared to that of native waxy corn starch. Gelatinisation enthalpy for those samples was slightly lower than for native corn starch. Prolonged illumination led to significant decrease in gelatinisation enthalpy from 9.65 J/g observed for native starch to 2.85 J/g found for sample WPLI-50. For this

Table 1
Melting temperatures and enthalpy for native and linear visible polarised light illuminated waxy corn starch (means of three independent experiments ± standard deviation; means within columns with different indices are significantly different at $P < 0.05$)

Sample	T_0 (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native	60.00 ± 1.12a	66.95 ± 0.21a	77.17 ± 1.16a	9.67 ± 1.13a,b,c
WPLI-5	59.99 ± 0.12a	66.94 ± 0.88a	76.33 ± 0.25a,b	6.86 ± 0.71d
WPLI-15	59.46 ± 0.31a	66.65 ± 0.41a	76.73 ± 0.91a,b	7.74 ± 0.71c,d
WPLI-25	58.39 ± 2.41a	66.85 ± 0.73a	76.63 ± 1.25a,b	7.95 ± 2.39b,c,d
WPLI-50	59.58 ± 0.77a	65.18 ± 0.25b	74.77 ± 1.55b,c	2.85 ± 0.92e
WPLN-50	60.00 ± 0.99a	66.80 ± 0.25a	77.15 ± 1.20a	9.50 ± 0.92a,b.c

sample, lower conclusion temperature (T_c) was also observed. Such results indicated that on illumination the crystalline structure of waxy corn starch granule underwent gradual disruption. It is worthy to note that illumination of native corn starch with visible polarised light (Fiedorowicz et al., 2001) leads to significant changes in their thermal properties.

3.2. Pasting properties

Pasting profiles of waxy corn starch illuminated in water analysed by RVA are shown in Fig. 1. Results are summarised in Table 2. Significant decrease in the paste viscosity could be observed for the sample illuminated for 50 h. This is accompanied by a change in melting enthalpy of this sample. When compared to that of control samples illuminated for 5, 15, and 25 h, these did not show any differences in the overall profile of viscosity curve and in all measured viscosities. This could indicate that slight changes in transition enthalpy observed for those samples reflects only minor changes in crystalline structure of starch granule after shorter illumination.

3.3. Iodine binding capacity

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

It was shown that the λ_{max} of starch iodine complexes depend 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 the extinction measured at 640 and 525 nm, respectively, could be regarded as a measure of the ratio of short

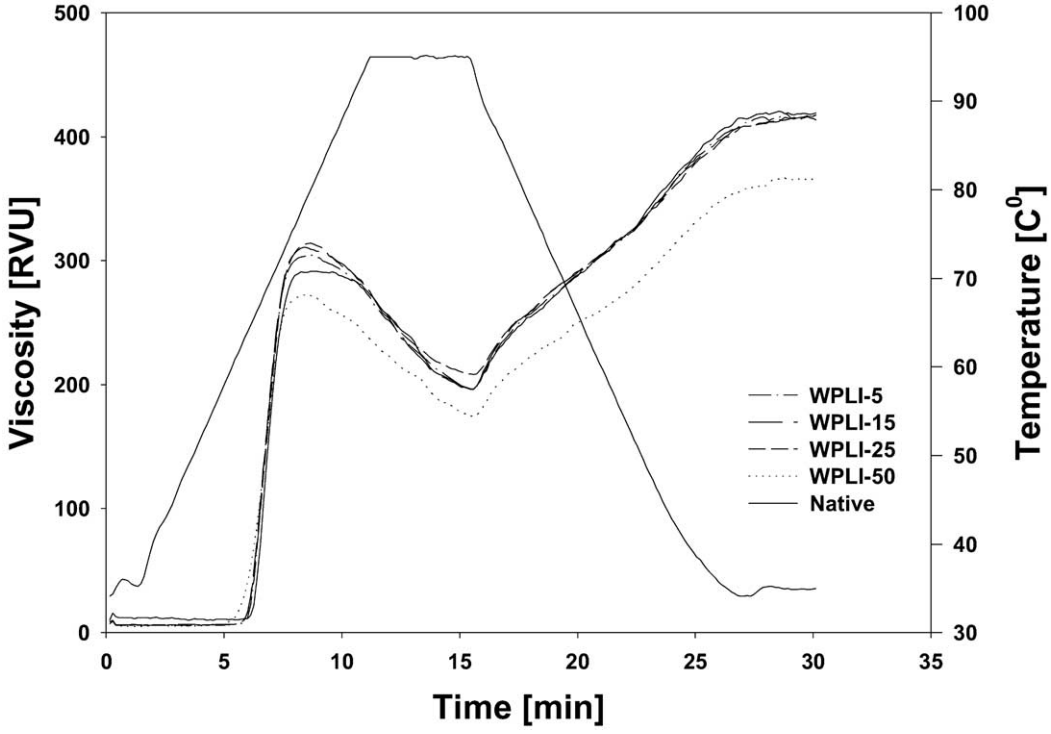

Fig. 1. Viscosity profiles obtained by Rapid Viscoanalyzer for waxy corn starch (native) and the starches illuminated for 5 (WPLI-5), 15 (WPLI-15), 25 (WPLI-25) and 50 (WPLI-50) h under nitrogen.

Table 2
Pasting properties of waxy corn starch (Native), and waxy corn starch kept in dark (WPLN) or illuminated with polarized light (WPLI)

Illumination[a] conditions	Pasting temperature (°C)	Peak viscosity (RVU)	Hold (RVU)	Final (RVU)	Time to peak (min)
Native	70.4	291.6	196.2	407.5	8.9
WPLI-5	70.4	304.7	195.6	403.9	8.8
WPLI-15	70.4	311.0	208.1	401.3	8.4
WPLI-25	71.0	314.0	208.1	400.0	8.7
WPLI-50	71.0	272.1	174.3	352.0	8.4
WPLN-50	70.4	292.0	196.0	405.6	8.9

[a] Numbers indicate treatment time.

chain branched (scb) and amylose-type non-branched/long-chain branched (nb/lcb) glucans.

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

In the case of amylopectin samples both BV and E_{640}/E_{525} ratio remained unchanged irrespective of illumination time. This could indicate that visible polarised light has no impact on corn amylopectin molecules. In the case of waxy corn starch, significant rise in BV and E_{640}/E_{525} ratio was observed for sample illuminated for 5 h. Further illumination led to gradual decrease in BV with the lowest value observed for sample illuminated for 50 h. Similar changes, although less pronounced, were observed for E_{640}/E_{525} ratio for this sample. It appears that although polysaccharide chains were disrupted by the cleavage of the valence glycosidic bonds, the overall macrostructure of the polysaccharide held by intra- and inter-molecular bonds remained.

3.4. Intrinsic viscosity

Intrinsic viscosity, $[\eta]$, for waxy corn starch and corn amylopectin samples illuminated with visible polarised light are listed in Table 3. As it was in the case of iodine binding properties, no differences in intrinsic viscosity values were observed for corn amylopectin samples irrespective of illumination time.

Gradual decrease in $[\eta]$ for waxy corn starch starch samples illuminated for 5 (WPLI-5), and 15 h (WPLI-15) were observed. Further illumination led to increase in intrinsic viscosity for sample WPLI-50 to the level observed for non-illuminated sample. The relationship between molecular weight, M_w and intrinsic viscosity $[\eta]$ is given by Mark–Houwink equation:

$$[\eta] = aM_w^b$$

where a and b are constants.

Numerous studies on viscosity behaviour of the solutions of native and processed starches were reported in literature (Dintzis & Bagley, 1995a,b; Dintzis, Bagley, & Felker, 1995; Hansen, Hoseney, & Faubion, 1991; Millard, Dintzis, Willet, & Klavons, 1997; Steenken, 1989) showing that starch samples of limited aqueous solubility follow Mark–Houwink relationship. Therefore, changes in intrinsic viscosities observed for illuminated waxy corn starch samples could be related to changes in molecular weight M_w of polysaccharide molecules constituting starch granule. Those changes correlate well with changes in molecular weight found by means of HPSEC-MALLS-RI analysis for native corn starch illuminated with polarised light (Fiedorowicz et

Table 3
Iodine binding properties and intrinsic viscosity values for waxy corn starch (Native), corn amylopectin (AP) and samples of waxy corn starch (WPLI) and corn amylopectin (APLI) illuminated with polarised light

Illumination conditions[a]	λ_{max} (nm)	BV	E_{640}/E_{525}	Intrinsic[b] viscosity $[\eta]$ (dl/g)
Native	528.6	0.076	0.78	7.9 ± 0.1
WPLI-5	525.4	0.104	1.06	7.5 ± 0.1
WPLI-15	528.8	0.086	0.66	5.9 ± 0.5
WPLI-25	527.6	0.071	0.66	6.6 ± 0.5
WPLI-50	529.6	0.030	0.64	8.0 ± 1.0
AP	540.6	0.056	0.55	4.3 ± 0.3
APLI-5	538.0	0.058	0.55	4.7 ± 0.3
APLI-15	539.0	0.055	0.57	5.1 ± 0.2
APLI-25	540.0	0.049	0.54	4.4 ± 0.3
APLI-50	540.2	0.049	0.54	4.6 ± 0.3

[a] Numbers indicate illumination time.
[b] Means of three independent experiments ± standard deviation.

al., 2001). Viscosity and IBC data observed for illuminated waxy corn starch samples support the former statement that initially the polarised light induce degradation of waxy corn starch polysaccharide molecules followed by cross-linking of resulted smaller molecules. Such a process leads to a sharp drop in ΔH value observed for sample WPLI-50 indicating major changes in the crystalline structure of starch granule. It is worthy to note that the polarised light inducing depolymerisation–repolymerisation reactions of polysaccharide molecules of normal corn (Fiedorowicz et al., 2001) did not lead to any change in the crystalline structure of starch granules. Data presented in this paper showed that the physicochemical properties of illuminated corn amylopectin are not affected by the polarised light. One could assume that the organised structures of polysaccharide chains, present as crystalline fragments in starch granule are necessary to induce photochemical reaction. According to the model proposed by Gallant et al. (1997) starch granule has alternating hard, crystalline, and soft semi-crystalline regions. They are organised in so-called blocklets. Recently, the existence and structure of the blocklets was confirmed by atomic force microscopy (Ohtani, Yoshino, Hagiwara, & Maekawa, 2000). The blocklets comprise of crystalline and amorphous lamellae. The model assumes that the crystalline lamellae consist of ordered double helical amylopectin side chain clusters. The latter are inter-leaved with more amorphous lamellae of the amylopectin branching regions.

Rundle and Baldwin (1943) and Rundle and French (1943) found that light with its electric vector parallel to the long axis of the helical amylose chains is strongly absorbed. Such a behaviour was explained by the fact that polarisability along extended amylose chain should be greater than that in the direction normal to the chain. Absorption of the energy of the polarised light by clusters of helical amylopectin side chains could generate vibrations in the crystalline lattice resulting in the bond cleavage i.e. in depolymerisation of the polysaccharide chains.

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