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Physicochemical properties of potato starch illuminated with visible polarised light

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Abstract

Suspensions (30%, w/w) of potato starch in pure water were illuminated for 5–50 h by linearly polarised visible light ($\lambda > 500$ nm) under stream of nitrogen. Effects of the illumination on the transition enthalpy, melting temperature, the pasting viscosity profiles, and iodine binding capacity of illuminated starch were examined. Starch illuminated in water for 50 h showed lower melting temperature T_p (60.57 °C) and transition enthalpy ΔH (10.01 J/g) than original potato starch soaked in water for the same period. After 25 h illumination in water the peak paste viscosity, P_v, of starch decreased in order to raise after 50 h illumination. Illumination in water initially degraded starch but prolonged illumination resulted in crosslinking into material of higher molecular weight. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Starch crosslinking; Starch depolymerisation; Starch repolymerisation

1. Introduction

Literature reports on the action of visible polarised light on starch are scarce and contradictory. Semmens (1947) attributed starch degradation caused by moonlight illumination to hydrolysing action of polarised light on starch. The same effect was responsible for increased germination in seeds with thin and transparent testa. However, according to Navez and Rubenstein (1928) degradation of starch in moonlight is enzymatic in its nature. Moonlight activates enzymes degrading starch. Recent findings (Hartmann & Mollwo, 1998) that star and moonlight stimulated germination of sensitised lettuce seeds suggest that the effect could be directly or indirectly related to degradation of starch playing a common role of energy reserve for plants. It has been shown in our recent paper (Fiedorowicz, Tomasik, & Lii, 2001) that illumination with polarised light of aqueous suspensions of cornstarch led initially to degradation of starch polysaccharide chains. Prolonged illumination induced crosslinking mainly in amylopectin chains. Mechanism of the action of polarised light on starch is unclear. We assumed that the light absorption by semicrystalline structures of starch granule was crucial for the initiation of degradation and following it crosslinking of polysaccharide chains.

Recently, Gallant, Bouchet, and Baldwin (1997) proposed new model of the structure of starch granule. Granule has alternating hard, crystalline, and soft, semicrystalline regions. They are organised in so-called blocklets. The blocklets comprise of alternating crystalline and amorphous lamellae. 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 was strongly absorbed. Such behaviour was explained by fact that polarisability along extended amylose chain should be stronger than in direction normal to the chain. Absorption of the energy of the polarised light in 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. It is known (Szczeniowski, 1972) that energy of the polarised light reflected on highly organised layers of a matter can be collimated. Gallant et al. (1997) suggested a high degree of organisation of the elements of starch granule in their model. Therefore, one can suppose that high organisation of starch granule might be an essential factor magnifying the effect of illumination. Such organisation can be specific for particular botanical origins of starch. Indeed, the effect of the UV radiation was different for starch granules of different starch varieties (Bertolini et al., 2001b).

In this work, we decided to examine effects of polarised light on potato starch being so different in structure and composition from cornstarch. Potato tuber starch has a

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Table 1
Melting temperatures and enthalpy of potato starch prior to (Native) and after illumination in water (PPLN), as well as starch soaked in water in the dark (DSK) as the reference sample (means of three measurements ± standard deviation; T_o = onset temperature, T_p = peak temperature, T_c = completion temperature, ΔH = melting enthalpy; means within column with different letters are different significantly at $P < 0.05$)

Sample[a]	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native	58.56 ± 0.27a,b	63.28 ± 0.41a,b,c	75.07 ± 0.85a	11.85 ± 0.63a
DSK-5	58.54 ± 0.20 a,b	63.10 ± 0.45a,b,c	75.20 ± 0.60a	11.86 ± 0.50a
DSK-15	58.20 ± 0.30a,b	63.15 ± 0.39a,b,c	75.13 ± 0.72a	11.53 ± 0.59a
DSK-25	58.30 ± 0.25a,b	63.20 ± 0.35a,b,c	75.08 ± 0.50a	11.70 ± 0.60a
DSK-50	58.50 ± 0.25a,b	63.25 ± 0.60a,b,c	75.01 ± 0.80a	11.75 ± 0.72a
PPLN-5	56.39 ± 0.13f	61.73 ± 0.02d	74.40 ± 1.77a	11.89 ± 0.42a
PPLN-15	57.03 ± 0.96e	62.84 ± 0.86c	74.93 ± 1.65a	11.35 ± 1.17a,b
PPLN-25	56.44 ± 0.21f	61.66 ± 0.13d	74.03 ± 0.60a	11.09 ± 0.96a,b
PPLN-50	54.59 ± 0.22g	60.57 ± 0.26e	71.27 ± 2.10b	10.01 ± 1.42b

[a] Numbers indicate treatment time (h).

high content of phosphate relative to cereal starches (Hizukuri, Tabata, & Nikuni, 1970; Rooke, Lampitt, & Jackson, 1949). Phosphate groups in starch reside in long chains of amylopectin (Blennow, Bay-Schmidt, Wischmann, Olsen, & Moller, 1998) at each ninth glucose units from the point of chain branching (Blennow et al., 1998; Takeda & Hizukuri, 1982).

2. Materials and methods

2.1. Illuminations

Slurries (250 ml, 30%) of *granular* potato starch (Polziem, Poznań, Poland) as well as D-glucose at the same concentrations in re-distilled water were illuminated from the distance of 30 cm. The 150 W xenon arc lamp XBO 150 (Oriel, England) with the slit illuminator KB 502 (Kabid, Chorzow, Poland) was the source of light. The HN 22 linear polarising filter (Polaroid, USA), with glass filter cutting off wavelengths below 500 nm was mounted between the slit illuminator and sample. 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).

Illuminations were carried out under nitrogen (5 ml/min) for 5, 15, 25 and 50 h at 25 °C. Nitrogen was passed through samples for 30 min prior to illumination. Illuminated samples were agitated using magnetic stirrer with 500 rpm rotor speed. After illumination samples were filtered on suction pump, then dried at 50 °C for 24 h.

Identically prepared starch suspensions agitated in the dark for 5, 15, 25 and 50 h served as control samples.

For glucose solutions, measurements of refraction index, specific rotation, and pH were performed using refractometer (Carl Zeiss, Jena, Germany), polarimeter (KB100 Kabid, Chorzow, Poland) and digital pH meter (N-512, Mera, Warsaw, Poland), respectively. Additionally NMR spectra (XL-300, Varian, Palo Alto, USA) were recorded for glucose, glucose kept in the dark and illuminated for 50 h. No changes in measured parameters were noted in illuminated D-glucose.

2.2. Thermal properties

Thermal properties of illuminated starch and control samples were determined by means of the differential scanning calorimeter (Setaram DSC 121, Setaram Co. France). The starch samples (1.5–2.0 mg) were sealed in aluminium pans 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.

2.3. Pasting properties

Pasting curves of native and illuminated potato starch (8%, w/w) were measured with rapid visco analyser (RVA, Newport Scientific, Newport, Australia). The starch suspensions were held 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 of 6 °C/min, and kept at 35 °C for 5 min.

2.4. Iodine staining

The blue value and λ_{max} of illuminated starches in the range of 500–800 nm 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% 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 of 200 mg of I_2 and 2 g of KI in 100 ml of distilled water. The mixture was brought to 100 ml with deionised water and mixed immediately. Blank solutions without starch were prepared identically.

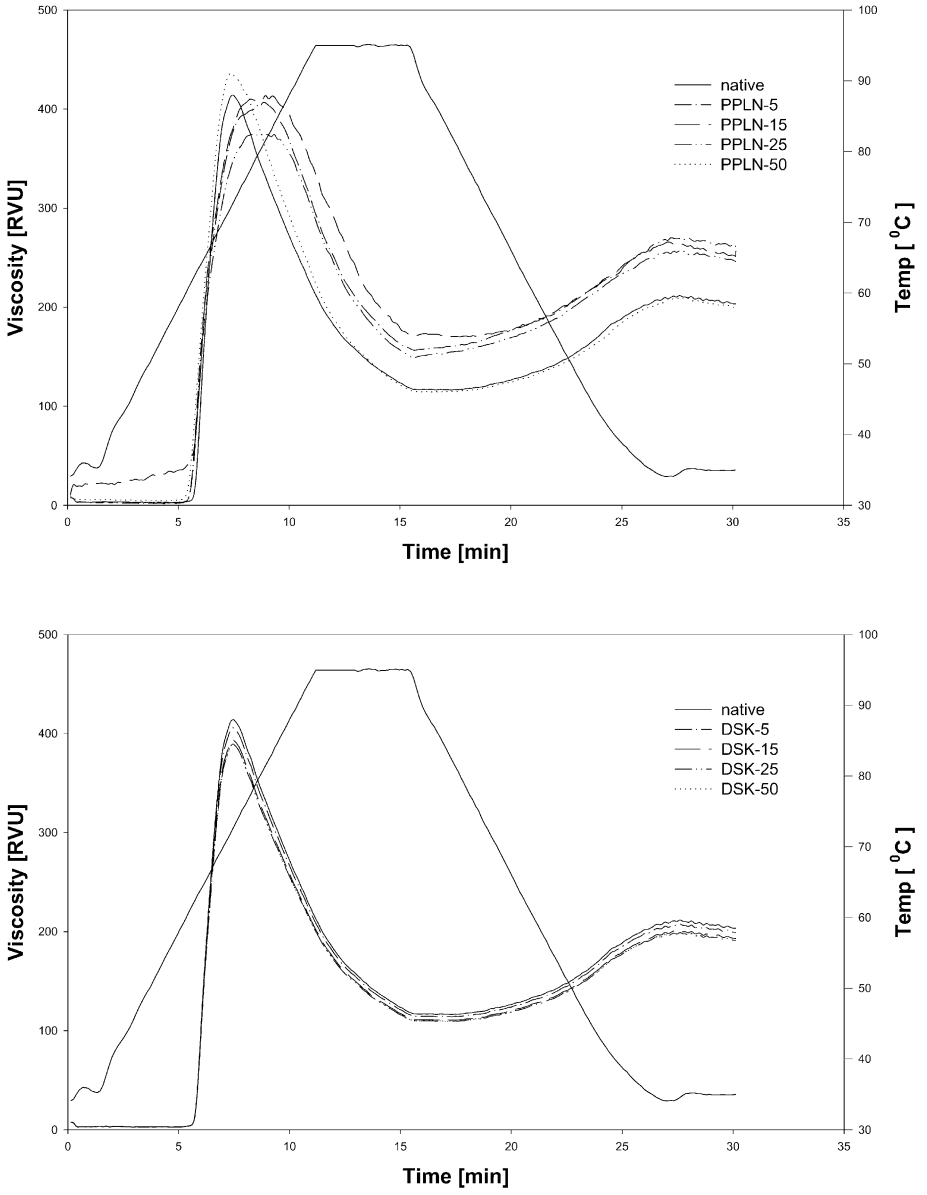

Fig. 1. (A) Pasting viscosity profiles of native potato starch and potato starch illuminated with polarised light in water for 5, 15, 25 and 50 h. (B) Pasting viscosity of native potato starch dark-soaked in water.

The blue value of starch–iodine complex 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. Thermal properties

Onset (T_o), peak (T_p), conclusion (T_c) and enthalpy (ΔH) for the gelatinisation of native, kept in the dark, and visible polarised light irradiated starches are listed in Table 1.

Illumination of aqueous potato starch suspensions for 50 h resulted in decrease in gelatinisation temperature of all samples. A slight, although statistically different, decrease was noted in gelatinisation enthalpy as compared to native starch. No significant differences in gelatinisation temperatures and gelatinisation enthalpy values could be seen for control starch samples stored in dark as well as for pregelatinised amylopectin (Fiedorowicz & Rębilas 2000). Moreover, illuminated aqueous solution of D-glucose did not change as indicated by refraction index and specific rotation. These findings documented that only crystalline samples could undergo changes on illumination with polarised light.

3.2. Pasting properties

Pasting profiles of potato starch illuminated in water

Table 2
Pasting properties of potato starch measured by RVA prior to (Native) and after illumination (PPLN)

Sample[a]	Pasting temperature[b] (°C)	Viscosity (RVU)[c,d]			Time to peak (min)
		Peak viscosity	Holding strength	Final	
Native	66.2	414.1	116.5	203.3	7.5
PPLN-5	65.5	406.3	156.8	251.3	8.8
PPLN-15	65.5	413.8	170.3	251.3	8.9
PPLN-25	65.5	375.1	152.7	246.0	8.7
PPLN-50	64.7	435.8	114.7	199.9	7.3

[a] Numbers indicate the illumination time.
[b] Standard deviations (SD) for all samples were below 3% of measured values.
[c] Measured in RVA units.
[d] Mean of triplicate experiment.

analysed by RVA are shown in Fig. 1A, and pasting profiles of control samples kept in dark are presented in Fig. 1B. Results are summarised in Table 2. Pasting profiles of the samples kept in dark were identical with the profile for native starch. For this reason, results of pasting of control samples are not quoted in Table 2. Peak viscosity of samples irradiated for 5 (PPLN-5), 15 (PPLN-15) and 25 (PPLN-25) h gradually decreased with illumination time from 414.0 to 375.1 RVU for native and PPLN-25, respectively. The 50 h-irradiation resulted in increase in the peak viscosity to 435 RVU (PPLN-50). Similar effect, although much more pronounced, was observed (Fiedorowicz et al., 2001) in RVA amylograms of normal cornstarch samples illuminated with polarised light in water. Such effect was explained by a degradation of polysaccharide chains followed, after prolonged illumination, by repolymerisation into chains of higher molecular weight. Changes observed in amylogram patterns described in our recent work suggested that similar process took place in similarly illuminated potato starch. Moreover, correlation between paste viscosity and molecular weight measured by SEC-MALLS-RI was found for cornstarch samples illuminated with polarised light (Fiedorowicz et al., 2001) and UV light (Fiedorowicz, Tomasik, You, & Lim, 1999). Similar correlations for paste viscosity (Bertolini, Mestres, & Colonna, 2000) and molecular weight (Bertolini et al., 2001b) of UV illuminated cassava and corn starches were reported by other authors. Therefore, we assumed that changes in pasting properties of illuminated potato starch described in this paper could be, to some extent, correlated with changes in molecular weight of polysaccharide chains constituting starch granule. Iodine staining properties of original starch prior to soaking, soaked in water in the dark and illuminated are given in Table 3.

Table 3
Iodine binding properties of native potato starch, starch soaked in water in the dark (DSK) and starch illuminated in water (PPLN)

Sample[a]	λ_{max}[b,c] (nm)	Blue value[c,d]	E_{640}/E_{525}
Native	602.0 ± 0.5	0.472 ± 0.005	1.31
DSK-5	601.5 ± 0.5	0.473 ± 0.005	1.31
DSK-15	602.0 ± 0.5	0.472 ± 0.005	1.31
DSK-25	601.5 ± 0.5	0.472 ± 0.010	1.31
DSK-50	602.0 ± 0.5	0.470 ± 0.005	1.31
PPLN-5	600.0 ± 0.5	0.454 ± 0.010	1.32
PPLN-15	598.6 ± 1.0	0.532 ± 0.040	1.41
PPLN-25	601.4 ± 0.6	0.480 ± 0.004	1.32
PPLN-50	597.2 ± 0.5	0.492 ± 0.006	1.28

[a] Numbers indicate the treatment time (h).
[b] Iodine binding wavelength maximum.
[c] Mean of three experiments ± standard deviation.
[d] Blue value is the absorbance of the starch–KI_5 complex measured at 640 nm.

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 correlated with rheological properties, freeze/thaw performance, and water binding properties of starches of different botanical origin. The sbc to nb/lcb ratio was expressed as the E_{640}/E_{525} ratio, where E was extinction measured at 640 and 525 nm, respectively. The λ_{max} of iodine complexes depended on the length of the glucan helices (Banks, Greenwood, & Khan 1971; Handa, Yaijima, Ishi, & Nishimura 1981). As λ_{max} asymptotically approached 640 nm for degree of polymerisation >200, values of iodine binding capacity, expressed as E_{640}/E_{525} ratio, exceeding 1.5 clearly pointed to the amylose type, nb/lcb, starch glucans (Bailey & Wehen, 1961; Pfannemüller, Mayerhofer, & Schulz, 1971).

Analysis of molar mass distribution of cornstarch illuminated by polarised light (Fiedorowicz et al., 2001) showed that formation of low molecular weight chains followed by their repolymerisation to longer chains proceeds preferably in the amylopectin fraction. Similar effect manifested by amylogram patterns was observed for illuminated potato starch. For potato starch illuminated in water, a raise in the blue value after 15 h was followed by decrease in that value after 50 h. Similar changes were noted in the E_{640}/E_{525} ratio. The results suggested formation of the amylose type, nb/lcb, glucan after 15 h of illumination followed by, at least partial, recombination of these molecules to branched chains.

We already reported similar depolymerisation followed by partial crosslinking of polysaccharide chains (Fiedorowicz et al., 1999) for cornstarch irradiated with UV light in aqueous suspensions. In the case of starch illuminated with UV light in the solid state (Bertolini et al., 2000; Bertolini, Mestres, Colonna, & Raffi, 2001a; Bertolini et al., 2001b) only degradation of starch polysaccharides was reported although formation of stable radicals was observed. The mechanism proposed by those authors for UV induced degradation of starch polysaccharides involved excitation of fluorescent chromophores at 360 and 290 nm in cassava starch and non-fluorescent chromophore at 320 nm in corn starch followed by breakage C_2–C_3 bond of glucopyranose. The intensity of ESR signal was lower when starch with higher water content was irradiated (Bertolini et al., 2001b). This could explain differences observed in UV induced reaction between starches irradiated in the solid state and in water. In the case of starch illuminated by polarised light either in solid state or in aqueous suspensions we did not observed any formation of radicals (Fiedorowicz, unpublished results). Moreover, no changes in intrinsic viscosity of DMSO solution of corn amylopectin illuminated with polarised light were observed (Fiedorowicz et al., 2000) indicating a lack of absorption of incoming light due to absence of chromophores in the visible part of UV–Vis spectrum. These observations support our thesis that absorption of polarised light by crystalline structures of starch granule could be responsible for the initiation of the depolymerisation—repolymerisation process. On the other hand it was shown that GBSSI (granule-bound starch synthase I) and SSII (starch synthase II) could elongate malto-oligosaccharides in isolated starch granules (Denyer, Waite, Motawia, Moller, & Smith, 1999). Similarly, starch branching enzyme I synthesised phosphorylated amylopectins in potato (Vikso-Nielesen, Blennow, Nielsen, & Moller, 1998). We could not exclude possibility that such granule-bound enzymes were activated by absorption of polarised light. Similar activation of Phytochrome A by low intensity moon and starlight was reported to be responsible for activation of germination of lettuce seeds (Hartmann & Mollwo, 1998). In order to exclude participation of such enzymes present in starch granules (Erlander, 1998) experiments with starch granules conditioned for 2 h at 120 °C were carried out in our former studies. Result of such deactivation of enzymes could be interpreted in two manners. Thus, either applied heat treatment activated enzymes or the action of polarised light on starch was caused by direct attack of light on polysaccharide. Activation of enzymes under applied conditions seemed to be unlikely. Moreover, starch samples kept in the dark and were illuminated and treated exactly in the same manner (and even simultaneously). Because no changes in measured physicochemical properties of starch kept in dark were noted we might assume that observed changes in illuminated samples were associated with direct action of polarised light on starch granule. This assumption was also accepted in our considerations in this paper. Natural light level during night time (full moon) measured as a spherical photon flux for the spectral range 400–700 nm is 10 nmol m^2 s^2 (Hartmann, Mollwo, & Tebbe, 1998) and is at least two orders of magnitude lower than that used in our experiments. It was shown that germination of the sensitised lettuce seeds was induced by 1 s exposition to the full moon (Hartmann & Mollwo, 1998). In our experiments much higher energy was needed to observe changes in starch properties, what supports our hypothesis about non-enzymatic way of the action of polarised light on starch granule.

4. Conclusions

Illumination with polarised light is suitable in modification of potato starch by depolymerisation of branched amylopectin and repolymerisation of abstracted short chains into longer non-branched chains. The effect of illumination is dependent on the starch variety and its crystallinity.

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