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Origin of defects in assembled supramolecular structures of sweet potato starches with different amylopectin chain-length distribution

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ABSTRACT

A combined approach of fluorophore-assisted capillary electrophoresis (FACEL), high-sensitivity differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), and light (LM) and scanning electron microscopy (SEM) was applied to study the effects of changes in amylopectin chain-length distribution on the assembly structures of sweet potato starches with similar amylose levels. It was shown that unlike ordinary sweet potato starch, starch extracted from Quick Sweet cultivar of sweet potato had anomalous high level of amylopectin chains with a degree of polymerization (DP) 6–12. Joint analysis of the obtained data revealed that amylopectin chains with DP 10–24 are, apparently, the dominant material for the formation of supramolecular structures in starch granules. In contrast, amylopectin chains with DP < 10 facilitated the formation of defects within crystalline lamellae. An increase in relative content of amylopectin chains with DP < 10 is accompanied by the correlated structural alterations manifested at all levels of starch granule organization (crystalline lamellae, amylopectin clusters, semi-crystalline growth rings, and granule morphology). Thus, the short amylopectin chains with DP < 10 were considered as an origin of the defectiveness in starch supramolecular structures.

1. Introduction

Starch is a semi-crystalline granular composite substance consisting of two α-glucan polysaccharides, namely, amylose and amylopectin. Biological objects, including starches, usually are the hierarchical ones; they consist of the different levels of supramolecular structuring, guaranteeing the biological functioning of the object. For starches, four types of supramolecular structures differing in macromolecular organization and characteristic sizes are well known. They are: crystalline and amorphous lamellae (~4–6 nm), amylopectin clusters (~9 nm), semi-crystalline, and amorphous rings (~120–400 nm), as well as granules themselves (~0.5–100 μm) (Buleon, Colonna, Planchot, & Ball, 1998; Imberty & Perez, 1988; Imberty, Chanzy, Perez, Buleon, & Tran, 1987, 1988; Jenkins & Donald, 1995; Jenkins, Cameron, & Donald, 1993; Koroteeva et al., 2007a, 2007b; Kozlov, Blennow, Krivandin, & Yuryev, 2007a; Kozlov et al., 2007b; Manners, 1989; Oostergetel & van Bruggen, 1993; Robin, Mercier, Charbonniere, & Guilbot, 1974; Sanderson, Daniels, Donald, Blennow, & Engelsen, 2006; Vandeputte & Delcour, 2004; Vermeylen, Goderis, Reynaers, & Delcour, 2004; Vermeylen et al., 2006; Waigh et al., 2000; Yuryev et al., 2004). Some models for the different levels of macromolecular organization in starch granules have been proposed. As a result, the "cluster" model giving an adequate description of the structure of amylopectin and normal starches is now considered as generally accepted. According to this model, the structural periodicity in semi-crystalline starch granules is formed by the repeating layers of amorphous background, including amylopectin and amylose macromolecules in unordered conformation, and semi-crystalline growth rings, consisting of alternating crystalline and amorphous lamellae. Crystalline lamellae consist of the double helices, formed from the short side chains of amylopectin macromolecules that are packed into two polymorphous forms with monoclinic (A-type) or hexagonal (B-type) packing. Amorphous lamellae contain amylose and longer amylopectin chains in unordered conformation.

In the last decade, many powerful methods of polymer physics have been applied to study the defects in starch supramolecular structures. It has been established that a formation of the defective structures occurs on all levels of macromolecular organization of starch polysaccharides. Amylose–lipid complexes or V-type crystalline structures, amylose "tie-chains, the defective ends of the

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double-helical chains dangling from crystallites into amorphous lamellae as well as amylopectin chains with a degree of polymerization (DP) 6–12 and 25–36 could be considered as the defects destabilizing structural organization crystalline lamellae (Bocharnikova et al., 2003; Fulton et al., 2002; Genkina, Kiseleva, Wasserman, & Yuryev, 2004a, Genkina, Wasserman, Noda, Tester, & Yuryev, 2004b; Genkina, Wikman, Bertoft, & Yuryev, 2007; Kiseleva et al., 2004, 2005; Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b; Nakamura et al., 2002; Noda, Kobayashi, & Suda, 2001; Noda, Nishiba, Sato, & Suda, 2003; Noda et al., 1998; Patindol & Wang, 2002; Singh, Isono, Srichuwong, Noda, & Nishinari, 2008; Vandeputte, Vermeylen, Geeroms, & Delcour, 2003; Yuryev et al., 2004). An accumulation of such defects within crystalline lamellae is accompanied, as a rule, by the decrease in the electronic density difference between amorphous and crystalline lamellae, and by the decrease in the melting temperature of crystalline lamellae as well (Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b; Yuryev et al., 2004). The total effect of amylose and amylopectin defects located within crystalline lamellae can be described by the means of Thomson–Gibbs' equation (Bocharnikova et al., 2003; Genkina et al., 2004a; 2007; Kiseleva et al., 2004, 2005; Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b; Yuryev et al., 2004). Generally, defectiveness of the double-helical packing within the crystals (non-ideal crystals) and of the crystallites within the crystalline lamellae (non-ideal integration) are the extremely important factors contributing to the melting temperature of starches. Unlike the defects located within the crystalline lamellae, an accumulation of amylose defects within the amorphous lamellae does not exert an influence on the starch melting temperature (Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b). The chain-length distribution of amylopectin also significantly influences the structures on the higher levels of granular organization. Particularly, the recent investigation showed that a degree of crystalline lamellae bending in B-type starches (starches with low level of short amylopectin chains) was sufficiently higher compared to the A-type starches (higher level of short amylopectin chains) (Sanderson et al., 2006). Additionally, the very long amylopectin chains could be, apparently, considered as proto-origins of the granular defects contributing to a formation of the cracked and remnant granules (Fulton et al., 2002; Koroteeva et al., 2007b). As assumed by Smith and co-authors (Fulton et al., 2002), the altered granule morphology could be caused, particularly, by the altered chain-length distribution of the short chains in amylopectin or by an increased proportion of the very long chains in amylopectin macromolecules.

Generally, analysis of the published data enables to propose that an alteration in the chain-length distribution of amylopectin and amylose content in starches can influence the formation of the defective supramolecular structures of different orders. However, with the exception of the recent published data for rice starches (Koroteeva et al., 2007a, 2007b), such investigations are limited, as a rule, by the study of one or maximum two levels of the structural organization of starch granules. Meanwhile, a lack of such data does not allow us to consider the abnormality in amylose or amylopectin structure as an origin of the defects in assembled supramolecular structures of different orders. Analysis of the published data (Katayama et al., 2002; Katayama, Tamiya, & Ishiguro, 2004) shows that the starch extracted from sweet potato breeding line of Kanto 116 could be a convenient object for such investigation.

In 2002, the Kanto 116 line was registered as a new sweet potato cultivar (Quick Sweet), presumably SSIIa deficient mutant. It was shown that compared with ordinary (normal) sweet potato starches, Quick Sweet starch had similar amylose level, but an anomalous high content of the extremely short amylopectin chains (DP 6–11), and a lower proportion of the chains with DP 12–28. Moreover, the starch from Quick Sweet cultivar was characterized by anomaly low melting temperature and altered (cracked) morphology of granule hilum (Katayama et al., 2002, 2004). It can be assumed that the marked changes in chain-length distribution of amylopectin could be the main reason exerting a significant influence on the thermodynamic parameters and the morphological features for Quick Sweet starch (Genkina et al., 2004b, 2003; Noda et al., 2001). However, it is worthy noting that the thermodynamic parameters of the starches were obtained in non-equilibrium conditions and the data of small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were absent. Hence, the effect of chain-length distribution of amylopectin on structural organization of the lamellar and cluster levels, as well as correlated alterations in starch supramolecular structures of higher order were not evaluated.

In the present work, the correlated alterations in the defectiveness of supramolecular structures caused by the differences in the chain-length distribution of amylopectin macromolecules of ordinary and mutant sweet potato starches are considered. For solution of the problem, the combined approach of fluorophore-assisted capillary electrophoresis (FACEL), high-sensitivity differential scanning calorimetry (DSC), WAXS, SAXS, and light (LM) and scanning electron microscopy (SEM) was used.

2. Materials and methods

2.1. Starch samples

Sweet potato starch with ordinary characteristics was purchased from Haraigawa Starch Factory, Kimotsuki Agricultural Cooperative Association, Kanoya, Kagoshima, Japan. Sweet potato cultivar "Quick Sweet" was grown at the experimental farm at the National Institute of Crop Science (NICS), Tsukuba, Ibaraki, Japan. Starch was extracted from Quick Sweet by using the previously described method (Noda, Takahata, Nagata, & Monma, 1992). Amylose content in starches was estimated from the blue value at 680 nm according to the modified method (Noda et al., 1992), eliminating the step of starch defatting.

2.2. Determination of amylopectin chain-length distribution by fluorophore-assisted capillary electrophoresis (FACEL)

Unit-chains of amylopectin ranged between DP 6 and 50 were analyzed by fluorophore-assisted capillary electrophoresis as described earlier (Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005). Analysis was performed in duplicate.

2.3. High-sensitivity differential scanning calorimetry (DSC)

Calorimetric investigations of starch dispersions in water (0.3% dry matter, sample volume 0.5 cm^3 in sealed cells) were performed using high-sensitivity differential scanning microcalorimeter DASM-4 (Puschino, Russia) over the temperature range of 10–120 °C with a heating rate of 2 K/min and excess pressure of 2.5 bar. Deionized water was used as a reference material. The heat capacity scale was calibrated using the Joule–Lenz effect for each run. As was shown previously, under the experimental conditions used, the corrections for dynamic lag and residence of the samples in calorimetric cell were not necessary, moreover, melting (gelatinization) of starch–water dispersions could be considered as quasi-equilibrium process (Danilenko, Shlikova, & Yuryev, 1994; Wang, Bogracheva, & Hedley, 1998). Additionally, for the starches with symmetric DSC-thermograms, the "two-state" model is applicable for a description of the melting process of crystalline lamellae (Bocharnikova et al., 2003; Danilenko et al., 1994; Genkina et al., 2003, 2004a, 2004b, 2007; Kiseleva et al., 2004, 2005; Koroteeva

et al. 2007a, 2007b; Kozlov et al., 2007a, 2007b; Yuryev et al., 2004). This model implies that there is a reversible transition between native and molten states. Accordingly, the parameter of cooperativity, which corresponds to the minimal number of the monomers undergoing the transition, could be determined (Bocharnikova et al., 2003; Danilenko et al., 1994; Genkina et al., 2003, 2004a, 2004b, 2007; Kiseleva et al., 2004, 2005; Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b).

Melting temperature (T_m) was attributed to the peak temperature on DSC-thermogram. The heat capacity jump (ΔC_p^{exp}) at the melting process was determined by the linearly extrapolation of the partial heat capacity change of the native C_p^n and the molten C_p^m states to the melting temperature T_m and was calculated as follows:

$$\Delta C_p^{exp} = C_p^m - C_p^n. \quad (1)$$

Calorimetric enthalpy (ΔH_m) was determined as the area under the peak above the extrapolation lines. The average values of the thermodynamic parameters were determined using five measurements at 95% significance level and normalized per mole of anhydroglucose units (162 g mol^{-1}). The error in determination of T_m is 0.2 K and the values of ΔH_m and ΔC_p^{exp} were determined with the error of not more than 5%. The procedure of the determination of thermodynamic melting parameters was detailed described elsewhere (Kozlov et al., 2007a).

The values of van Hoff enthalpy (ΔH^{vH}) were calculated accordingly to previously published papers (Bocharnikova et al., 2003; Danilenko et al., 1994; Genkina et al., 2003, 2004a, 2004b, 2007; Kiseleva et al., 2004, 2005; Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b).

$$\Delta H^{vH} = 2T_m R^{1/2}(C_p - 0.5\Delta C_p^{exp})^{1/2}, \quad (2)$$

where R is gas constant, T_m is the melting temperature of starch crystalline lamellae, C_p is the difference between the maximum ordinate on the DSC-thermogram and the value of C_p^n, linearly extrapolated to the melting temperature T_m. The values for the parameter of cooperativity (v) and the thickness of crystalline lamellae (L_{crl}) were calculated accordingly to the following equations:

$$v = (\Delta H^{vH})/(\Delta H_m) \quad (3)$$

$$L_{crlDSC} = 0.35v, \quad (4)$$

where ΔH_m is the experimental melting enthalpy of crystalline lamellae, ΔH^{vH} is the van Hoff enthalpy and the pitch height per anhydroglucose residue in the double helix is 0.35 nm (Gernat, Radosta, Anger, & Damaschun, 1993).

According to the theory for semi-crystalline synthetic polymers (Bershtein & Egorov, 1994), the melting temperature of crystallites (T_m) can be calculated using the Thomson–Gibbs' equation:

$$T_m = T_m^0[1 - 2\gamma_i/(\Delta H_m^0 \rho_{crl} L_{crl})] \quad (5)$$

where T_m^0 and ΔH_m^0 are, the melting temperature and the melting enthalpy of a hypothetical crystal with unlimited size, γ_i is the free surface energy of crystalline lamellae face side, while ρ_{crl} and L_{crl} are the density and the thickness of the crystal, respectively. The values for γ_i were estimated using the T_m^0 = 366.5 K, ΔH_m^0 = 35.5 J/g and ρ_{crl} = 1.48 g/cm^3 for A-type spherulitic crystals (Whittam, Noel, & Ring, 1990) and T_m^0 = 346.8 K, ΔH_m^0 = 35.5 J/g and ρ_{crl} = 1.40 g/cm^3 for B-type spherulitic crystals (Whittam et al., 1990), as well as the mean L_{crlDSC} value for the investigated starches estimated using Eq. (4).

For asymmetric DSC-endotherms of starch melting in 0.6 M KCl solution, a deconvolution procedure of the experimental DSC-curves was applied, assuming that the independent melting processes of the individual crystallites of A- and B-type polymorphs could be approximated by Gaussian functions (Genkina et al., 2003, 2004b). The peak fit program (PeakFit v4.12 for Windows, SYSTAT Software Inc.) was used for the experimental DSC-curves deconvolution and for the calculation of the thermodynamic parameters obtained as a result of deconvolution. The relative content of the individual polymorphic structures was estimated from the enthalpy contributions of these structures as a result of a deconvolution of the total calorimetric peak.

2.4. Wide-angle X-ray scattering (WAXS)

Wide-angle X-ray scattering measurements of starch powders from ordinary and Quick Sweet cultivars of sweet potato were carried out using the X-ray diffractometer of local design supplied with one-dimensional position-sensitive detector constructed in Joint Institute of Nuclear Research (Dubna, Russia) (Cheremukina et al., 1990). X-ray patterns were recorded in transmission geometry with CuK_α radiation and were plotted as functions of $S = (2\sin\theta)/\lambda$, where λ is CuK_α-wavelength (0.1542 nm) and θ is a half of a scattering angle.

Relative crystallinity (C), i.e. the weight percent of crystalline part in a starch sample, was assessed with WAXS patterns as

$$C = \frac{\int [I(S) - I_a(S)]S^2 dS}{\int I(S)S^2 dS} \times 100\%. \quad (6)$$

In this expression, $I(S)$ is the intensity of the starch sample, $I_a(S)$ is the intensity of the reference amorphous starch sample normalized so that it closely approach the intensity of the starch sample at $S \approx 2.4$ nm^{-1}; the integration was carried out over the interval from S = 0.5 nm^{-1} to S = 3.5 nm^{-1}. The reference samples of amorphous starches were prepared by 6 h milling of sweet potato starches. It was found that for ordinary sweet potato starch C = 30%, while for Quick Sweet starch C = 18%.

2.5. Small-angle X-ray scattering (SAXS)

For SAXS measurements the powders of native starches were dispersed in distilled water to form slurries (~50% w/w) according to previous works (Koroteeva et al., 2007a; Kozlov et al., 2007a, 2007b; Yuryev et al., 2004). SAXS measurements were carried out in transmission geometry using the X-ray diffractometer designed in the Institute of Biochemical Physics. During X-ray exposure, the starch slurries were kept in sealed cells to prevent dehydration. The X-ray beam emitted from the fine-focus Cu X-ray tube (30 kV/30 mA) was line-focused with a glass mirror. The SAXS patterns were recorded with a one-dimensional position-sensitive detector. Experimental SAXS curves were corrected for the background scattering, corrected (desmeared) for collimation distortions and plotted as a function of $S = (2\sin\theta)/\lambda$, with λ and 2θ being the CuK_α-wavelength (0.1542 nm) and the scattering angle, respectively. Collimation correction was performed with the SAXS-data processing program "PRO", developed in the Institute of Crystallography of Russian Academy of Sciences (Moscow, Russia). Intensity of SAXS peak (I_{max}) was determined by the graphical method as described elsewhere (Yuryev et al., 2004). Desmeared SAXS curves were also analyzed according to paracrystalline one-dimensional lamellar stack model, as described elsewhere (Jenkins & Donald, 1995; Yuryev et al., 2004) and the average size of amylopectin cluster (L_{amcl}) and the crystalline lamellar thickness ($L_{crlSAXS}$) were estimated.

2.6. Light (LM) and scanning electron microscopy (SEM)

Starches were suspended in distilled water (8% w/w) and the suspension poured on a microscopic glass was observed in LM microscope OLYMPUS BX60 in polarized light using Nomarski

contrast (Błaszczak et al., 2003). In the case of SEM, dry granules were deposited on a copper disc and coated with gold using the Jeol JEE-400 vacuum evaporator. The specimens were examined by the means of scanning electron microscope Jeol 5200 at 10 kV accelerating voltage.

3. Results and discussion

The profiles of the molar distribution of amylopectin unit-chains for starches of ordinary sweet potato and Quick Sweet are shown in Fig. 1. The chromatographic profiles are classified according to Hanashiro, Abe, and Hizukuri (1996) into four groups named fa, fb_1, fb_2, and fb_3, respectively (Fig. 1), of which fb_3 corresponds to the long B-chains of DP $\geqslant$ 37 and the others are the sub-groups of the short amylopectin chains. As can be seen from Fig. 1, the chain-length distribution for ordinary sweet potato starch is characterized by the maximum at DP 12–13, which is typical for sweet potato starches. In contrast, the drastic increase in the relative content of chains with DP 6–12, as well as the significant decrease in the relative content of fb_1 fraction (DP 13–24) corresponding to the mixture of longer A-chains and short B1-chains was detected for starch from the Quick Sweet cultivar. Fraction fa (DP 6–12) corresponds mostly to the short A-chains. Fractions fb_2 (DP 25–36) and fb_3 (DP > 37), corresponding to the chains interconnecting the building blocks inside the clusters (Bertoft, 2004, 2007) were found in variable amounts for both samples. Generally, the molar distribution of amylopectin unit-chains for Quick Sweet starch is characterized by anomalous high content of amylopectin chains with DP 6–12 and a lower level of the chain population with DP 13–24 compared with the corresponding sub-fractions of amylopectin chains in ordinary sweet potato starch (Fig. 1). This conclusion is in accordance with the earlier published data for Quick Sweet and other sweet potato starches (Katayama et al., 2002).

Original DSC-curves related to gelatinization of aqueous sweet potato starch dispersions (Fig. 2) demonstrate the typical endothermic transitions attributed to a melting of starch crystalline lamellae. The thermodynamic melting parameters of crystalline lamellae for sweet potato starches with ordinary and increased

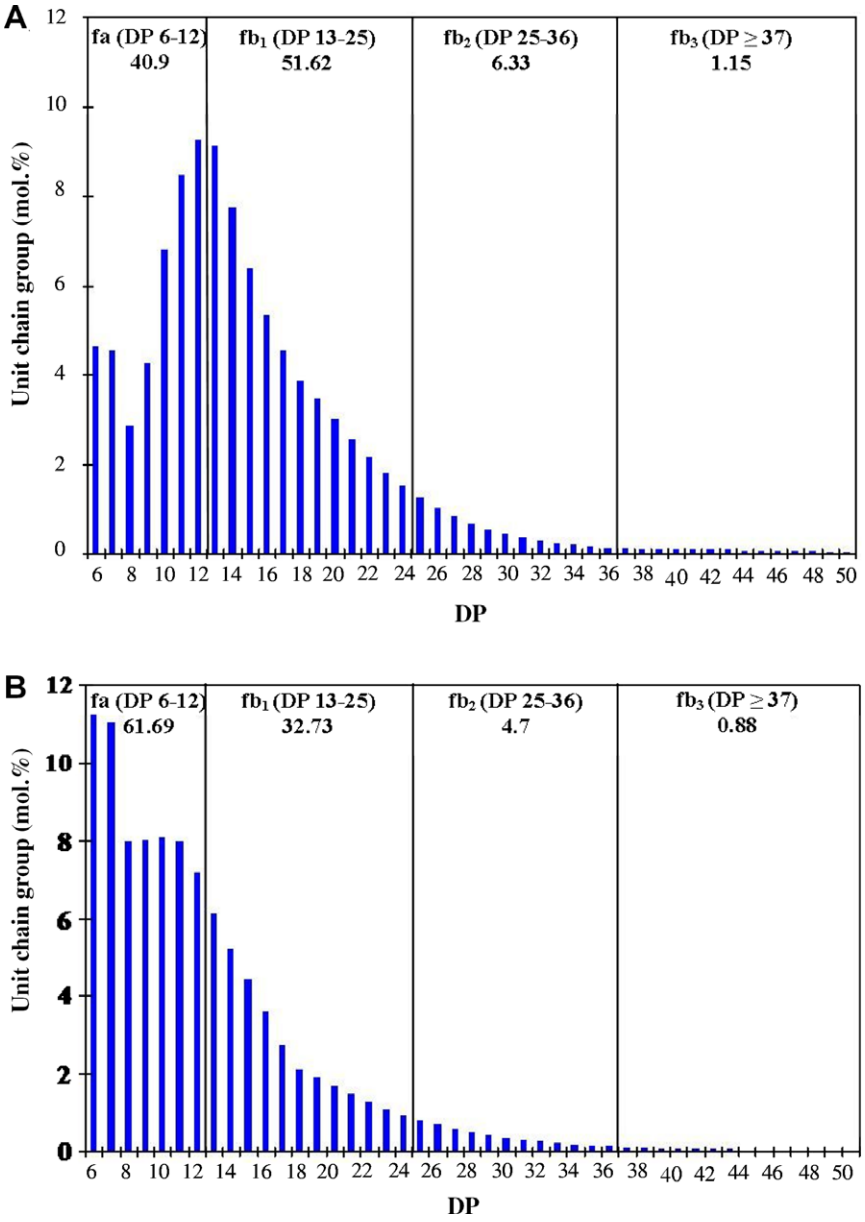

Fig. 1. Profiles of the molar distribution of amylopectin unit-chains for starches extracted from ordinary (A) and Quick Sweet (B) cultivars of sweet potatoes.

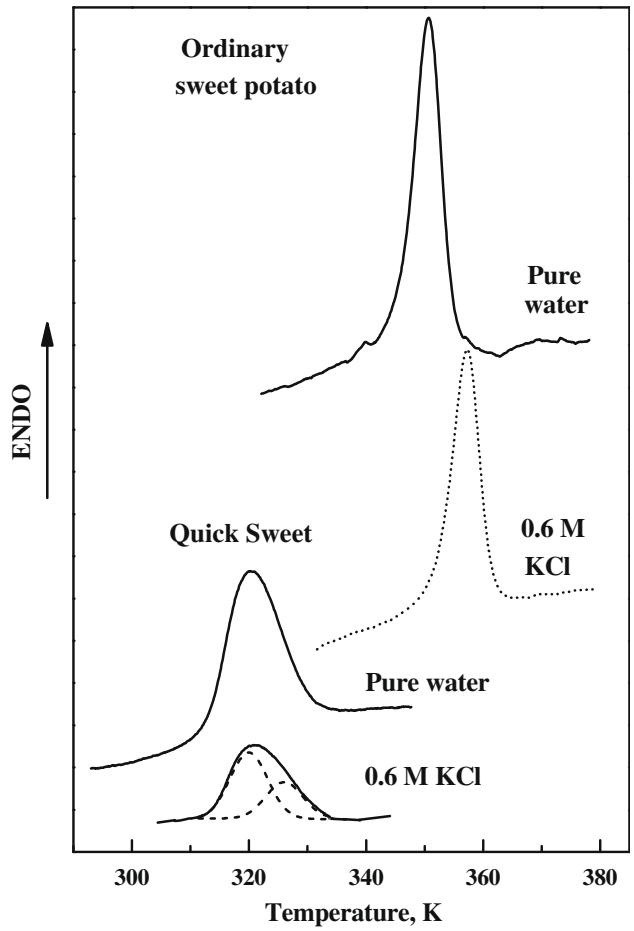

Fig. 2. DSC-traces for native sweet potato starches in pure water and in 0.6 M KCl solution.

content of amylopectin chains with DP 6–12 (Fig. 2 and Table 1) are in general agreement with previously published data (Katayama et al., 2002). Some differences could be, particularly, due to the variations in the environmental conditions during plant maturation (Genkina et al., 2003, 2004b; Noda et al., 2001) and/or the differences between the concentration of dispersions used in earlier published thermodynamic experiments (Katayama et al., 2002) and in our investigation. The presented investigations were carried out at quasi-equilibrium conditions (Danilenko et al., 1994; Wang et al., 1998) (low concentration – 0.3% on dry matter and heating rate – 2 K min^{-1}), while the concentrations applied in other works (Katayama et al., 2002) were 30% on dry matter. Analysis of the experimental data (Fig. 2 and Table 1) reveals the decreasing value as for the melting enthalpy, as for the melting temperature of crystalline lamellae for Quick Sweet starch contrary to ordinary starch.

From the thermodynamic point of view, the chains decreasing T_m and ΔH_m values could be attributed to the defects destabilizing the structure of crystalline lamellae, whereas the chains, increasing the thermodynamic parameters, could be ascribed to ones promoting a suboptimal packing within the crystalline lamellae. Hence, the chains forming the double helices and crystallites, have to show a positive correlation between T_m (ΔH_m) values and their relative amount in starches, as it was shown, for example, for some other starches (Fulton et al., 2002; Koroteeva et al., 2007b; Nakamura et al., 2002; Noda et al., 1998, 2003; Patindol & Wang, 2002; Singh et al., 2008; Vandeputte et al., 2003). The combined analysis of the chromatographic and DSC data (Figs. 1 and 2; Table 1) demonstrates a negative relation between the T_m (ΔH_m) values and the relative amount of the amylopectin chains with DP 6–11, while for amylopectin chains with higher degree of polymerization the reverse picture is observed. It could be assumed therefore, that amylopectin chains with DP 6–12 are related to the chains "dangling" from amorphous into crystalline lamellae (Genkina et al., 2007; Koroteeva et al., 2007b), destabilizing, thereby, the latter. Unlike the chains with DP 6–12, the amylopectin chains with DP > 12 could be considered as the chains participating in the formation of double helices and starch crystals.

According to the theory for semi-crystalline polymers (Bershtein & Egorov, 1994) and the practice of its application for starches (Genkina et al., 2004a, 2007; Kiseleva et al., 2004, 2005; Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b), the alterations in the melting temperature of semi-crystalline polymers, including starches, can be described by using Thomson–Gibbs' equation (Eq. (5), see in Section 2). Analysis of the Eq. (5) shows, that the melting temperature is a function of three following variables: the polymorphous structure of starch (T^0_m, ρ_{crl}), the thickness of crystalline lamellae (L_{crl}) and free surface energy of crystallite face side (γ_i). The γ_i value is mainly governed by the surface entropy (S_i) that is proportional to the content of the defects (Bershtein & Egorov, 1994).

Using the Eqs. (1)–(4), the cooperative melting unit (ν) and the thickness of crystalline lamella (L_{crlDSC}) for the starches can be calculated from the calorimetric data (Table 2) (Bocharnikova et al., 2003; Danilenko et al., 1994; Genkina et al., 2003, 2004a, 2004b, 2007; Kiseleva et al., 2004, 2005; Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b; Vermeylen et al., 2006). Taking into account the errors in the determination of the ν and L_{crl} values one can see that the ν and L_{crlDSC} values are similar for both investigated starches. It enables to evaluate the average values of these parameters. The calculation shows (Table 2) that the average values for the cooperative melting unit and the thickness of crystalline lamellae are 10.4 ± 0.9 anhydroglucose residues and 3.6 ± 0.2 nm, respectively. Similar results for the ν and L_{crlDSC} values were obtained for the starches extracted from some Italian wheat cultivars (Wasserman et al., 2006), though these values are less than the corresponding values usually obtained for different A- or B-type starches, as well as for the other sweet potato starches (Bocharnikova et al., 2003; Danilenko et al., 1994; Genkina et al., 2003, 2004a, 2004b, 2007; Kiseleva et al., 2004, 2005;

Table 1
Melting temperatures (T_m) and melting enthalpies (ΔH_m) of crystalline lamellae of sweet potato starches in pure water and in 0.6 M KCl as well as the content of A- (CA) and B- (CB) type structures in crystalline lamellae.

Starch type	Amylose content (%)	T_m (K)		ΔH_m (kJ/mol)		CA (%)	CB (%)
		In pure water	In 0.6 M KCl	In pure water	In 0.6 M KCl		
Ordinary	23.7	350.7	357.3	4.9	3.05	100	–
Quick Sweet	19.2	320.3	320.0* 326.0**	3.3	1.2* 0.7**	34.8	65.2

The T_m and ΔH_m values for Quick Sweet starch in 0.6 M KCl are indicated for low (*) and high (**) temperature melting peaks, respectively.

Table 2
Cooperative melting unit (ν), thickness of crystalline lamellae (L_{crlDSC}) and free surface energy of crystal face side (γ_i) for sweet potato starches.

Starch type	ν (anhydroglucose residues)	L_{crlDSC} (nm)	γ_i (10^7/J cm^{-2})
Ordinary	11.0	3.7	4.94
Quick Sweet	9.7	3.4	7.65
Mean value	10.4 ± 0.9	3.6 ± 0.2	

Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b; Vermeylen et al., 2006; Yuryev et al., 2004). Nevertheless, the average value of the cooperative melting unit (10.4 ± 0.9 anhydroglucose residues) is close to the minimal degree of polymerization of glucose residues (DP 10–12) capable to form B- or A-type polymorph crystals (Gidley & Bulpin, 1987; Pfannemüller, 1987) and is similar to the minimal amount, namely 12, of anhydroglucose residues corresponding to one of two single strands in amylopectin double helix, according to the geometry proposed by O'Sullivan and Pérez (1999). Finally, the average ν value is in accordance with the evaluation obtained from the joint DSC- and chromatographic data (see above). Summing up these data, it could be concluded that minimal DP of amylopectin chains capable to form the crystalline structures in sweet potato starches is 10–11 anhydroglucose residues, while amylopectin chains with DP < 10 could be apparently considered as the defects with respect to starch crystalline structures.

This conclusion agrees well enough with the WAXS data for the investigated starches. As can be seen from Fig. 3, the intensity of crystalline reflexes and a degree of crystallinity for sweet potato starch with anomalous high content of shorter amylopectin chains (Quick Sweet) is significantly lower compared to the corresponding data for the starch with ordinary distribution of amylopectin chains (Fig. 1). Generally, analysis of the calorimetric data (Table 1) shows that the alterations in chain-length distribution of amylopectin in sweet potato starches do not exert influence on the values of the cooperative melting unit and the thickness of crystalline lamellae, but leads to the changes in their internal lamellar structure (in particular, degree of defectiveness of crystalline lamellae).

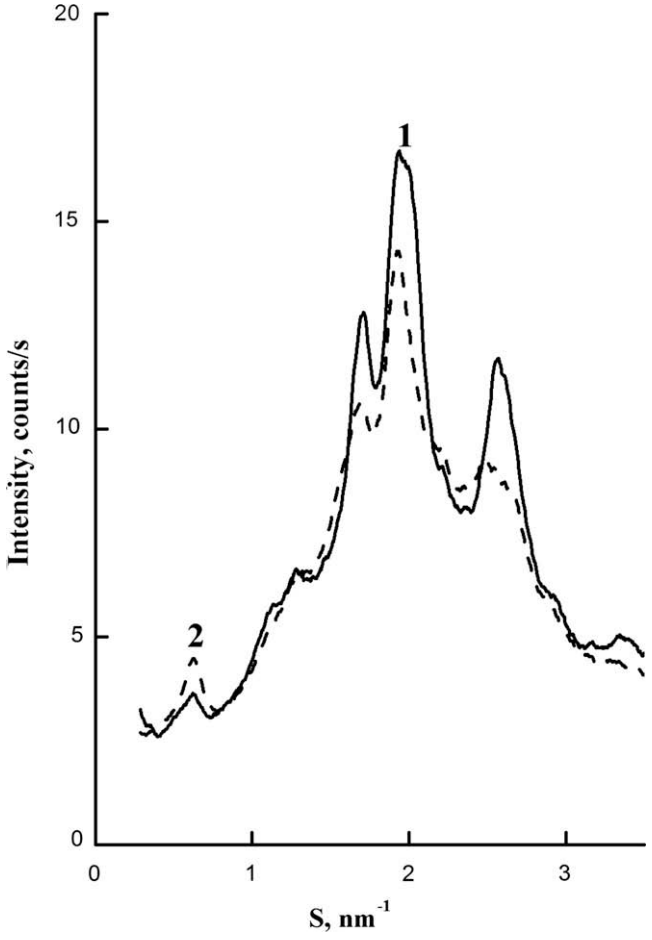

Fig. 3. WAXS patterns of sweet potato starches with ordinary (1) and increased (2) levels of amylopectin chains with DP < 10.

The detailed identification of the position of crystalline reflexes and the determination of their ratio show that the diffractograms (Fig. 3) of the investigated starches are typical for C (A + B) type structure. However, the A:B ratios of these structures in starches are different. This result is expected since recently it was shown that the differences in ratio of A- and B-crystalline structures in sweet potato starches could be depended, particularly, on the differences in growth temperature for the investigated cultivars of sweet potato (Genkina et al., 2003, 2004b). Comparing the hereinabove data with the earlier published X-ray data for the starches with A- and B-type packing of amylopectin chains in starch crystals (Imberty & Perez, 1988; Imberty et al., 1987, 1988), it could be concluded that sweet potato starch with ordinary distribution of amylopectin contains mainly A-type crystalline structures, while the starch with anomalous high content of shorter amylopectin chains contains both A- and B-type crystalline structures. For the quantitative evaluation of the content of these polymorphous structures in the investigated starches, the additional calorimetric investigations and analysis of the data should be carried out. This analysis was developed for C-type pea starches (Pfannemüller, 1987; Wang et al., 1998) and was previously applied to the study of the crystalline structure of other C-type sweet potato starches (Genkina et al., 2003, 2004b). The approach is based on the following points: (i) T_m of A- and B-type starches increases at 7–10 K (normal maize) and at 1–4 K (potato starch), respectively, in the presence of 0.6 M KCl, compared to the corresponding data in pure water (Pfannemüller, 1987; Wang et al., 1998), (ii) for C-type starches one asymmetric melting peak or two divided melting peaks are observed in 0.6 M KCl, the lower one being attributed to B-type polymorph and the higher to A-type (Pfannemüller, 1987; Wang et al., 1998). Since the melting enthalpy of the ordered structures in polymers is proportional to their amounts (Bershtein & Egorov, 1994), the content of A- and B-type structures for C-type starches could be calculated as the individual enthalpy contributions from of A- and B-structures to the total melting enthalpy using a deconvolution procedure of the complex calorimetric peak (Genkina et al., 2003, 2004b). The calorimetric investigations of sweet potato starches in 0.6 M KCl reveal that sweet potato starch with ordinary distribution of amylopectin chains can be attributed at first approach to the starches containing mainly A-type crystalline structures, whilst sweet potato starch with anomalous high content of shorter amylopectin chains can be identified as C-type starch containing 34.8% of A-type and 65.2% B-type crystalline structures.

Despite the presence of the weak crystalline reflex at $2\Theta = 5.6^{o}$ revealing an insignificant amount of B-type structures in normal sweet potato starch (Fig. 3), the conclusion based on the DSC data (Table 1) generally agrees with the WAXS data. It follows that in order to evaluate the γ_i values (see Thomson–Gibbs' equation, Section 2) for sweet potato starch with ordinary distribution of amylopectin chains, T_m^0 and ρ_{crl} values for A-type spherolitic crystals could be used, while for sweet potato starch with anomalous high content of shorter amylopectin chains, T_m^0 and ρ_{crl} values should be calculated as:

$$T_m^0 = T_{mA}^0 \cdot \alpha_A + T_{mB}^0 \cdot \alpha_B \quad (7)$$

$$\rho_{crl} = \rho_{crlA} \cdot \alpha_A + \rho_{crlB} \cdot \alpha_B, \quad (8)$$

where $T_{mA}^0, T_{mB}^0, \rho_{crlA}$ and ρ_{crlB} are, respectively, the melting temperatures and the densities for A- and B-type spherulitic crystals, α_A and α_B present the relative contents of these polymorphic structures in starch. The calculation demonstrates a significant increase in the γ_i values for Quick Sweet starch as compared to normal sweet potato starch (Table 2). Since γ_i values are mainly governed by the surface entropy that is proportional to the content of the defects (Bershtein & Egorov, 1994), it could be assumed that an increase in the content of short amylopectin chains (DP 6–10) is accompa-

nied by a significant increase of the defectiveness of crystalline lamellae. Summing up the data, it could be concluded, that the amylopectin chains with DP < 10 destabilize the ordered organization of the crystalline lamellae, reflected in the changes of thermodynamic melting parameters. Moreover, it could be expected that the alterations in the structural organization of crystalline lamellae would affect the structure of amylopectin clusters, as well.

The SAXS patterns of the investigated starches are shown in Fig. 4. The presented diffraction profiles are at the same relative scale and therefore are directly comparable. As can be seen from Fig. 4, the profile and the intensity of SAXS peak (I_{max}) for the starch with ordinary distribution of amylopectin chains are typical both for amylopectin and normal starches (Jenkins & Donald, 1995; Jenkins et al., 1993; Koroteeva et al., 2007a; Kozlov et al., 2007b; Sanderson et al., 2006; Vermeylen et al., 2004, 2006; Waigh et al., 2000; Yuryev et al., 2004). In contrast, the I_{max} value for sweet potato starch with anomalous high content of shorter amylopectin chains is much lower, being similar to the corresponding value for rice starches with a high defectiveness (Koroteeva et al., 2007a). Let us now look in more details on the alterations of I_{max} values (Table 3). According to the recently published data (Koroteeva et al., 2007a; Kozlov et al., 2007a, 2007b; Yuryev et al., 2004), a decrease in the electronic density difference between crystalline and amorphous lamellae can be referred to an accumulation of amylose and amylopectin defects (amylose "tie-chains or shorter amylopectin chains, for example). Taking into consideration that (i) the level of amylose "tie-chains" depends on the total content of amylose macromolecules in starches (Bocharnikova et al., 2003; Koroteeva et al., 2007a, 2007b; Kozlov et al., 2007a, 2007b; Yuryev et al., 2004), (ii) the difference in amylose content for the investigated starches is not so large (Table 1), (iii) the endothermic transitions typical for amylose–lipid complexes or V-type crystals are absent on the DSC-curves of starches (Fig. 2), and (iv) the level of defectiveness of crystalline lamellae, caused by shorter amylopectin chains is anomalously high (Table 2), it could be assumed that the main contribution to a decrease of I_{max} values is introduced by the defects from amylopectin chains with DP < 10. According to the earlier published data (Genkina et al., 2007; Koroteeva et al., 2007a, 2007b), such chains "dangle" inside crystalline lamellae from amorphous lamellae and decrease, thereby, the density of the macromolecular packing in crystalline lamellae. It promotes a decrease in the electronic density difference between crystalline and amorphous lamellae. The parameters of amylopectin clusters for the investigated starches were determined on the basis of SAXS-data analysis using Wolf–Bragg equation and the paracrystalline diffraction theory (Table 3). The values of the thickness of amylopectin clusters calculated from Wolf–Bragg's equation for both starches are, generally, similar. Moreover, they are in accordance with the corresponding data for wheat (Kozlov et al., 2007b; Yuryev et al., 2004) and rice (Koroteeva et al., 2007a) starches. Unfortunately, the application of one-dimensional paracrystalline model for the description of SAXS peaks has allowed evaluation of the crystalline lamellae thickness and amylopectin cluster size for normal sweet potato starch only (Table 3). For sweet potato starch with anomalous high content of shorter amylopectin chains, the values of structural parameters were significantly overestimated and were considered unreasonable. The thickness of amylopectin clusters determined by the paracrystalline approach for ordinary sweet potato starch (Table 3) was smaller compared to the value calculated using Wolf–Bragg equation. Generally, such a result is expected since similar data were obtained earlier for wheat (Kozlov et al., 2007b; Yuryev et al., 2004) and rice (Koroteeva et al., 2007a) starches. Finally, this calculated value is practically equal to the corresponding data for A-, B-. and C-type starches (Jenkins & Donald, 1995; Jenkins et al., 1993; Koroteeva et al., 2007a; Kozlov et al., 2007a, 2007b; Sanderson et al., 2006; Vermeylen et al., 2004, 2006; Waigh et al., 2000; Yuryev et al., 2004). Additionally, the value of the crystalline lamellae thickness for ordinary sweet potato starch obtained at SAXS-data analysis (Table 3) is in accordance with the corresponding value calculated from DSC data using the "two-state" model (Table 2). Generally, summing up the SAXS and DSC data, it could be concluded that the alterations in the internal structure of crystalline lamellae and amylopectin clusters observed at passing from ordinary starch to one with anomalous high content of shorter amylopectin chains, do not affect the sizes of the supramolecular structures.

The microscopic observations made under polarized light indicate also some significant differences in the internal structure of granules for two investigated starches. The granules of normal sweet potato starch demonstrate the typical birefringence pattern under polarized light (Fig. 5A), whilst for the starch with anomalous high content of shorter amylopectin chains (Fig. 5C) the different picture was observed. One can see that the majority of the granules show a lack of Maltese cross at the hilum area, while

Table 3
The intensity maximum (I_{max}) of SAXS peak, thickness of amylopectin clusters (L_{amcl}) and crystalline lamellae ($L_{crlSAXS}$) for sweet potato starches.

Starch type	I_{max} (counts/s)	L_{amcl}* (nm)	L_{amcl}** (nm)	$L_{crlSAXS}$** (nm)
Ordinary	12.5	10.5	9.0	4.0
Quick Sweet	1.7	9.4	–	–

* Values calculated from Wolf–Bragg's equation.
** Values calculated from paracrystalline model.

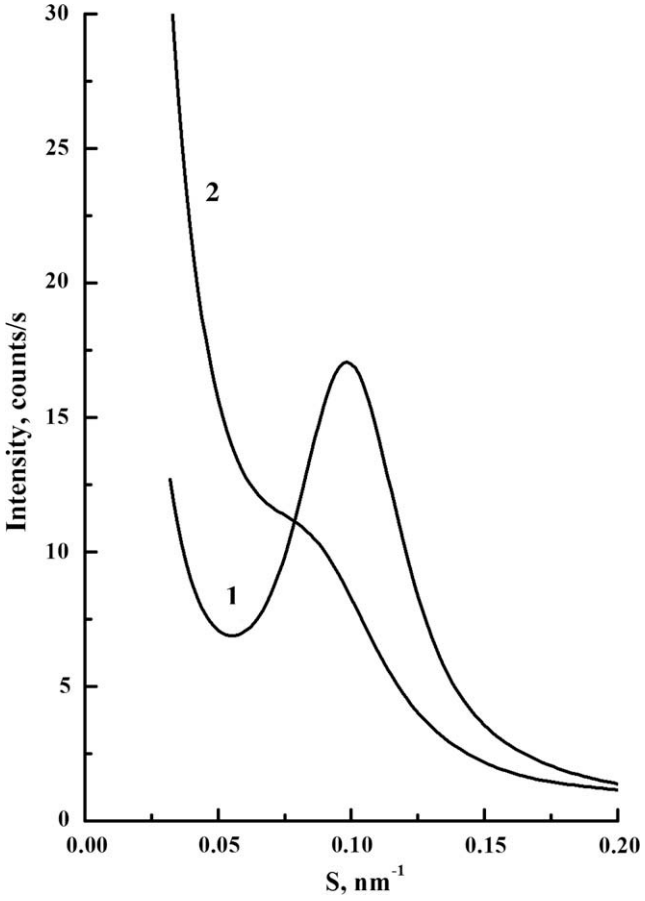

Fig. 4. Desmeared SAXS curves for sweet potato starches with ordinary (1) and increased (2) levels of amylopectin chains with DP < 10.

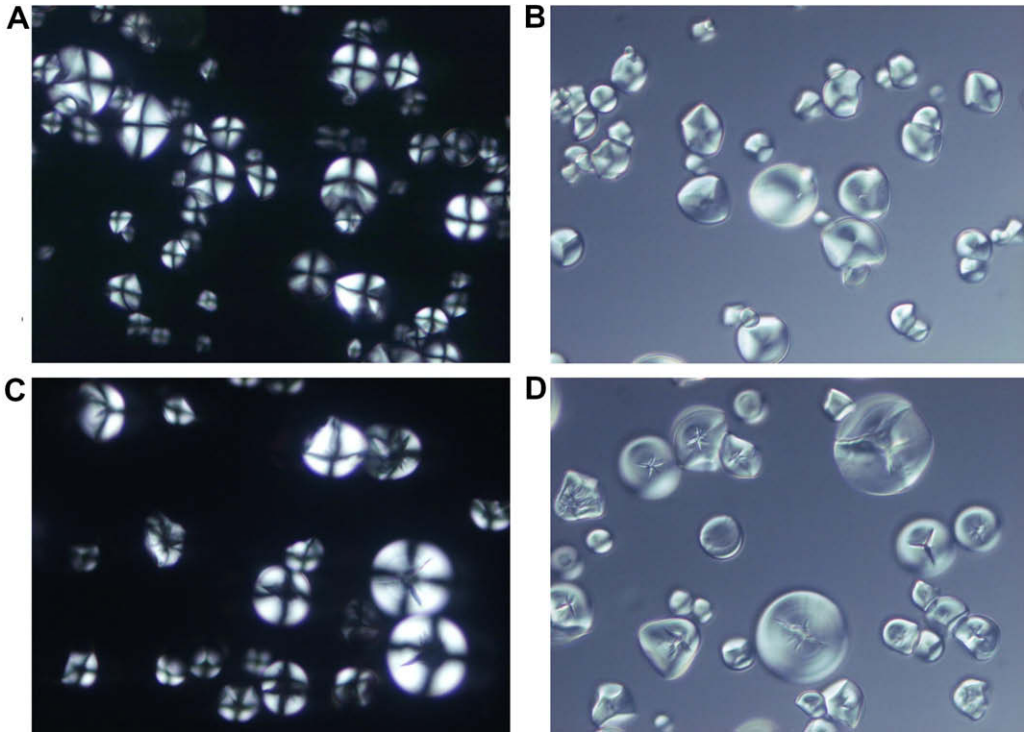

Fig. 5. LM photos of native sweet potato starches with ordinary (A and B) and increased levels (C and D) of amylopectin chains with DP < 10 (A) and (C) were obtained in polarized light.

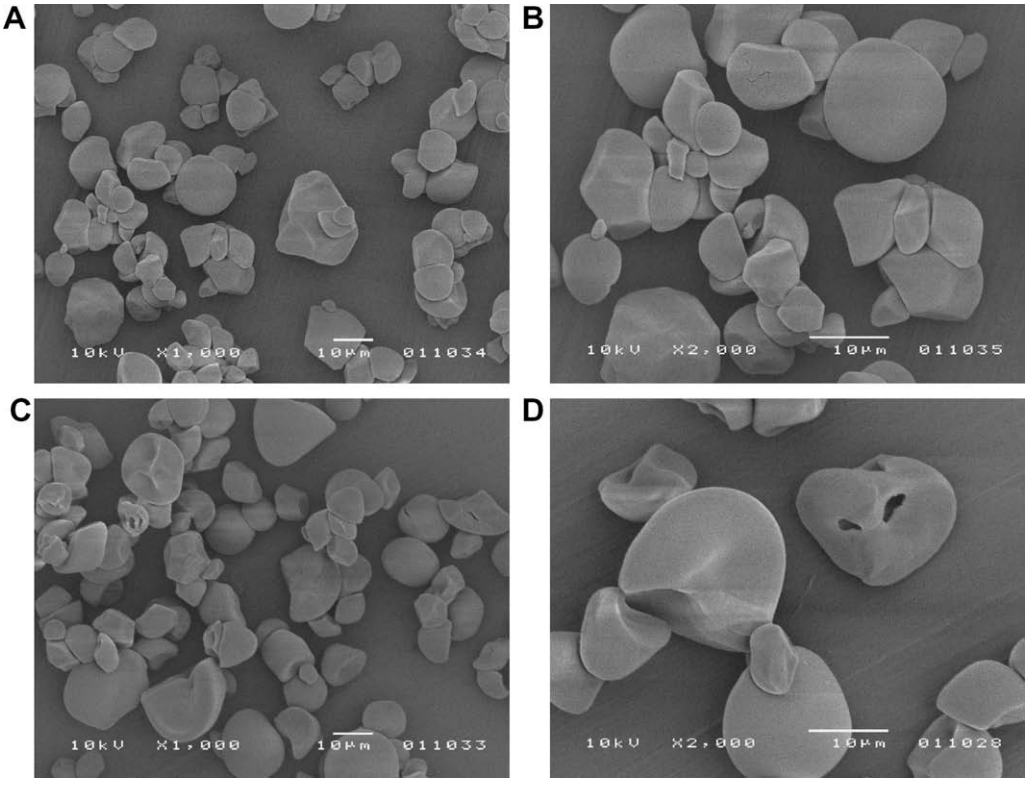

Fig. 6. SEM photos of native sweet potato starches with ordinary (A and B) and increased levels (C and D) of amylopectin chains with DP < 10.

external parts of the granules still display birefringency. Also, a few cracks are found at the hilum region. Additionally, the differences in the morphology of the centers of individual granules can be seen (Fig. 5B and D), with some granules revealing more significant disruption (cracking) than others. On the basis of the presented results it could be assumed that the differences in the internal

structure of starch granules, the localization of the cracks in the granule, and a change in Maltese cross at the hilum area are evoked by the different distribution and/or concentration of the defects caused by increasing content of amylopectin chains with DP < 10 in sweet potato starches. Apparently, the same defects appear on the level of the whole granule, as it is evident from the SEM images of starches (Fig. 6). One can see that sweet potato starch with ordinary distribution of amylopectin chains demonstrates typical round, polygonal, and spherical shapes of the granules with the sizes ranged from 5 to 25 μm (Fig. 6A and B). Generally, the granules of ordinary sweet potato starch are characterized by rather smooth and non-cracked surface, while the starch granules with abnormally high content of shorter amylopectin chains have distorted morphology with some cracks and holes on the surface (Fig. 6C and D).

4. Conclusions

The combined approach of FACEL, DSC, WAXS, SAXS, LM, and SEM demonstrated the defectiveness of supramolecular structures on the different levels (crystalline lamellae, amylopectin clusters, semi-crystalline growth rings, and granules) in sweet potato starches with similar amylose content but altered chain-length distribution of amylopectin. Analysis of the data implied the marked contribution of shorter amylopectin chains with DP < 10 to the defectiveness of starch supramolecular structures. An accumulation of such chains in the internal structure of the granule of sweet potato starches led to the following effects: (i) decrease in the melting enthalpy of crystalline lamellae, as well as a degree of starch crystallinity and the electronic density differences between crystalline and amorphous lamellae, and (ii) formation of the cracks on the surface and inside the granules. Besides, accumulation of shorter amylopectin chains with DP < 10 in sweet potato starches promotes the increase in the defectiveness of starch supramolecular structures, which is manifested at all levels of granular organization. Finally, it can be concluded that the abnormal amylopectin chain-length distribution (increase in the content of shorter chains) is an important factor responsible for the defectiveness of supramolecular structures in starch granules.

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References

Bershtein, V. A., & Egorov, V. M. (1994). Differential scanning calorimetry of polymers. In T. J. Kemp (Ed.), *Physics, chemistry, analysis, technology* (pp. 1–253). New York: Ellis Horwood.

Bertoft, E. (2004). On the nature of categories of chains in amylopectin and their connection to the supper helix model. *Carbohydrate Polymers, 57*, 211–224.

Bertoft, E. (2007). Composition of building blocks in clusters from potato amylopectin. *Carbohydrate Polymers, 70*, 123–136.

Błaszczak, W., Valverde, S., Fornal, J., Amarowicz, R., Lewandowiz, G., & Borkowski, K. (2003). Changes in the microstructure of wheat, corn and potato starch granules during extraction of non-starch compounds with sodium dodecyl sulfate and mercaptoethanol. *Carbohydrate Polymers, 53*, 63–73.

Bocharnikova, I. I., Wasserman, L. A., Krivandin, A. V., Fornal, J., Błaszczak, W., Chernykh, V. Ya., et al. (2003). Structure and thermodynamic melting parameters of wheat starches with different amylose content. *Journal of Thermal Analysis and Calorimetry, 74*, 681–695.

Buleon, A., Colonna, P., Planchot, V., & Ball, S. (1998). Starch granules: Structure and biosynthesis. *International Journal of Biological Macromolecules, 23*, 85–112.

Cheremukina, G. A., Chernenko, S. P., Ivanov, A. B., Pashekhonov, V. D., Smykov, L. P., & Zanevsky Yu, V. (1990). Automatized one-dimensional X-ray-detector. *Isotopenpraxis, 26*, 547–549.

Danilenko, A. N., Shlikova, Ye. V., & Yuryev, V. P. (1994). Equilibrium and cooperative unit of the process of melting of native starches with different packing of the macromolecular chains in the crystallites. *Biophysics, 39*, 427–432.

Fulton, D. C., Edwards, A., Pilling, E., Robinson, H. L., Fahy, B., Seale, R., et al. (2002). Role of granule-bound starch synthase in determination of amylopectin structure and starch granule morphology in potato. *The Journal of Biological Chemistry, 277*, 10834–10841.

Genkina, N. K., Noda, T., Koltisheva, G. I., Wasserman, L. A., Tester, R. F., & Yuryev, V. P. (2003). Effects of growth temperature on some structural properties of crystalline lamellas in starches extracted from sweet potatoes (*Sunnyred* and *Ayamurasaki*). *Starch/Stärke, 55*, 350–357.

Genkina, N. K., Kiseleva, V. I., Wasserman, L. A., & Yuryev, V. P. (2004a). Evaluation and classification of starch crystalline imperfection through annealing. Retrospective analysis. In P. Tomasik, V. P. Yuryev, & E. Bertoft (Eds.), *Starch: Progress in structural studies modifications and applications* (pp. 115–134). Malopolska Branch, Cracow: Polish Society of Food Technologists.

Genkina, N. K., Wasserman, L. A., Noda, T., Tester, R. F., & Yuryev, V. P. (2004b). Effect of annealing on the polymorphic structure of starches from sweet potato grown at various soil temperatures. *Carbohydrate Research, 339*, 1093–1098.

Genkina, N. K., Wikman, J., Bertoft, E., & Yuryev, V. P. (2007). Effects of structural imperfection on gelatinization characteristics of amylopectin starches with A- and B-type crystallinity. *Biomacromolecules, 8*, 2329–2335.

Gernat, C., Radosta, S., Anger, H., & Damaschun, G. (1993). Crystalline parts of three different conformations detected in native and enzymatically degraded starches. *Starch/Stärke, 45*, 309–314.

Gidley, M. J., & Bulpin, P. V. (1987). Crystallization of maltooligosaccharides as models of the crystalline forms of starch: Minimum chain length requirement for the formation of double helices. *Carbohydrate Research, 161*, 291–300.

Hanashiro, I., Abe, J.-I., & Hizukuri, S. (1996). A periodic distribution on the length of amylopectin as revealed by high-performance anion-exchange chromatography. *Carbohydrate Research, 283*, 151–159.

Imberty, A., Chanzy, H., Perez, S., Buleon, A., & Tran, V. (1987). New three-dimensional structure for A-type starch. *Macromolecules, 20*, 2634–2636.

Imberty, A., Chanzy, H., Perez, S., Buleon, A., & Tran, V. (1988). The double helical nature of the crystalline part of A-starch. *Journal of Molecular Biology, 201*, 365–378.

Imberty, A., & Perez, S. (1988). A revisit to the three dimensional structure of B-type starch. *Biopolymers, 27*, 1205–1221.

Jenkins, P. J., Cameron, R. E., & Donald, A. M. (1993). A universal feature in the structure of starch granule from different botanical sources. *Starch/Stärke, 45*, 417–420.

Jenkins, P. J., & Donald, A. M. (1995). The influence of amylose on starch granule structure. *International Journal of Biological Macromolecules, 17*, 315–321.

Katayama, K., Komae, K., Kohyama, K., Kato, T., Tamiya, S., & Komaki, K. (2002). New sweet potato line having low gelatinization temperature and altered starch structure. *Starch/Stärke, 54*, 51–57.

Katayama, K., Tamiya, S., & Ishiguro, K. (2004). Starch properties of new sweet potato lines having low pasting temperature. *Starch/Stärke, 56*, 563–569.

Kiseleva, V. I., Genkina, N. K., Tester, R., Wasserman, L. A., Popov, A. A., & Yuryev, V. P. (2004). Annealing of normal, low and high amylose starches extracted from barley cultivar grown under different environmental conditions. *Carbohydrate Polymers, 56*, 157–168.

Kiseleva, V. I., Krivandin, A. V., Fornal, J., Blaszczak, W., Jelinski, T., & Yuryev, V. P. (2005). Annealing of normal and mutant wheat starches. LM, SEM, DSC and SAXS studies. *Carbohydrate Research, 340*, 75–83.

Koroteeva, D. A., Kiseleva, V. I., Krivandin, A. V., Shatalova, O. V., Błaszczak, W., Bertoft, E., et al. (2007a). Structural and thermodynamic properties of rice starches with different genetic background. Part 2: Defectiveness of different supramolecular structures in starch granules. *International Journal of Biological Macromolecules, 41*, 534–547.

Koroteeva, D. A., Kiseleva, V. I., Sriroth, K., Piyachomkwan, K., Bertoft, E., Yuryev, P. V., et al. (2007b). Structural and thermodynamic properties of rice starches with different genetic background. Part 1: Differentiation of amylopectin and amylose defects. *International Journal of Biological Macromolecules, 41*, 391–403.

Kozlov, S. S., Blennow, A., Krivandin, A. V., & Yuryev, V. P. (2007a). Structural and thermodynamic properties of starches extracted from GBSS and GWD suppressed potato lines. *International Journal of Biological Macromolecules, 40*, 449–460.

Kozlov, S. S., Krivandin, A. V., Shatalova, O. V., Noda, T., Bertoft, E., Fornal, J., et al. (2007b). Structure of starches extracted from near isogenic wheat lines Part II: Molecular organization of amylopectin clusters. *Journal of Thermal Analysis and Calorimetry, 87*, 575–584.

Manners, D. J. (1989). Recent development in our understanding of amylopectin structure. *Carbohydrate Polymers, 11*, 87–112.

Nakamura, Y., Sakurai, A., Inaba, Y., Kimura, K., Iwasawa, N., & Nagamine, T. (2002). The fine structure of amylopectin in endosperm in Asian cultivated rice can be largely classified into two classes. *Starch/Stärke, 54*, 117–131.

Noda, T., Takahata, Y., Nagata, T., & Monma, M. (1992). Digestibility of sweet potato raw starches by glucoamylase. *Starch/Stärke, 44*, 32–35.

Noda, T., Takahata, Y., Sato, T., Suda, I., Morishita, T., Ishiguro, K., et al. (1998). Relationship between chain length distribution of amylopectin and

gelatinization properties within the same origin for sweet potato and buckwheat. *Carbohydrate Polymers, 37*, 153–158.
Noda, T., Kobayashi, T., & Suda, I. (2001). Effect of soil temperature on starch properties of sweet potatoes. *Carbohydrate Polymers, 44*, 239–246.
Noda, T., Nishiba, Y., Sato, T., & Suda, I. (2003). Properties of starches from several low-amylose rice cultivars. *Cereal Chemistry, 80*, 193–197.
Oostergetel, G. T., & van Bruggen, E. F. J. (1993). The crystalline domains in potato starch granules are arranged in in a helical fashion. *Carbohydrate Polymers, 21*, 7–12.
O'Sullivan, A. C., & Pérez, S. (1999). The relationship between internal chain length of amylopectin and crystallinity in starch. *Biopolymers, 50*, 381–390.
Patindol, J., & Wang, Y. J. (2002). Fine structures of starches from long-grain cultivars with different functionality. *Cereal Chemistry, 79*, 465–469.
Pfannemüller, B. (1987). Influence of chain length of short monodisperse amyloses on the formation of A-type and B-type X-ray diffraction patterns. *International Journal of Biological Macromolecules, 9*, 105–108.
Robin, J. P., Mercier, C., Charbonniere, R., & Guilbot, A. (1974). Litnerized starches. Gel-filtration and enzymatic studies of insoluble residues from prolonged acid treatment of potato starch. *Cereal Chemistry, 51*, 389–406.
Sanderson, J. S., Daniels, R. D., Donald, A. M., Blennow, A., & Engelsen, S. B. (2006). Exploratory SAXS and HPAEC-PAD studies of starches from diverse plant genotypes. *Carbohydrate Polymers, 64*, 433–443.
Singh, N., Isono, N., Srichuwong, S., Noda, T., & Nishinari, K. (2008). Structural, thermal and viscoelastic properties of potato starch. *Food Hydrocolloids, 22*(6), 979–988.
Srichuwong, S., Sunarti, T. C., Mishima, T., Isono, N., & Hisamatsu, M. (2005). Starches from different botanical sources I: Contribution of amylopectin fine structure to thermal properties and enzyme digestibility. *Carbohydrate Polymers, 60*, 529–538.
Vandeputte, G. E., Vermeylen, R., Geeroms, J., & Delcour, J. A. (2003). Rice starches. I. Structural aspects provide insight into crystallinity characteristics and gelatinization behaviour of granular starch. *Journal of Cereal Science, 38*, 43–52.
Vandeputte, G. E., & Delcour, J. A. (2004). From sucrose to starch granule to starch physical behaviour: A focus on rice starch. *Carbohydrate Polymers, 58*, 245–266.
Vermeylen, R., Goderis, B., Reynaers, H., & Delcour, J. A. (2004). Amylopectin molecular structure reflected in macromolecular organization of granular starch. *Biomacromolecules, 5*, 1775–1786.
Vermeylen, R., Derycke, V., Delcour, J. A., Goderis, B., Reynaers, H., & Koch, M. H. J. (2006). Gelatinization of starch in excess water: Beyond the melting of lamellar crystallites. A combined wide- and small-angle X-ray scattering study. *Biomacromolecules, 7*, 2624–2630.
Waigh, T. A., Kato, K. L., Donald, A. M., Gidley, M. G., Clarke, C. J., & Riekel, C. (2000). Side-chain liquid-crystalline model for starch. *Starch/Stärke, 52*, 450–460.
Wang, T. L., Bogracheva, T. Y., & Hedley, C. L. (1998). Starch: As simple as A, B, C? *Journal Experimental Botany, 49*, 481–502.
Wasserman, L. A., Vaccino, P., Boggini, G., Schiraldi, A., Noda, T., Kudryavzev, A. M., et al. (2006). Electrophoretic and DSC studies on different wheat starches with various amylose contents. *Polish Journal of Food and Nutrition Sciences, 15*(56), 59–66.
Whittam, M. A., Noel, T. R., & Ring, S. (1990). Melting behaviour of A- and B-type crystalline starch. *International Journal of Biological Macromolecules, 12*, 359–362.
Yuryev, V. P., Krivandin, A. V., Kiseleva, V. I., Wasserman, L. A., Genkina, N. K., Fornal, J., et al. (2004). Structural parameters of amylopectin clusters and semi-crystalline growth rings in wheat starches with different amylose content. *Carbohydrate Research, 339*, 2683–2691.