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Effects of annealing on the polymorphic structure of starches from sweet potatoes (*Ayamurasaki* and *Sunnyred* cultivars) grown at various soil temperatures

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Abstract—Starches extracted from the sweet potato cultivars *Sunnyred* and *Ayamurasaki* grown at 15 or 33 °C (soil temperature) were annealed in excess water (3 mg starch/mL water) for different times (1, 4, 8 or 10 h) at the temperatures 2–3 K below the onset melting temperature. The structures of annealed starches, as well as their gelatinisation (melting) properties, were studied using high-sensitivity differential scanning calorimetry (HSDSC). In excess water, the single endothermic peak shifted to higher temperatures, while the melting (gelatinisation) enthalpy changed only very slightly, if any. The elevation of gelatinisation temperature was associated with increasing order/thickness of the crystalline lamellae. The only DSC endotherm identified in 0.6 M KCl for *Sunnyred* starch grown at 33 °C was attributed to A-type polymorphic structure. The multiple endothermic forms observed by DSC performed in 0.6 M KCl for annealed starches from both cultivars grown at 15 °C provided evidence of a complex C-type (A- plus B-type) polymorphic structure of crystalline lamellae. The A:B-ratio of two polymorphic forms increased upon annealing due to partial transformation of B- to A-polymorph, which was time dependent. Long heating periods facilitated the maximal transformation of B- to A-polymorph associated with limited A:B ratio.

Keywords: Starch; Annealing; Crystalline polymorphs; Crystalline lamellae; Thermodynamic properties

1. Introduction

Physicochemical properties of starches are dependent on their composition, polysaccharide structure and supramolecular organisation. It has been determined (for wheat) that starch polymeric composition (amylopectin/amylose ratio) is controlled by specific biosynthetic enzymes that have both genetic and environmental regulation.[1–3] The biosynthetic events controlling starch supramolecular features such as formation of crystalline and amorphous phases, their interactions, thickness and perfection are not understood. Since starch from every plant type has specific types of crystalline packing of its amylopectin double helices (based on A- or B-type unit cells), it is evident that the formation of crystalline regions is under genetic control. On the other hand, the observed structural changes associated with variations of growth conditions during plant maturation point out the existence of the environmental regulation, too. The relationship between these aspects is not clear and is therefore worthy of investigation.

It has been shown that increasing soil temperature during sweet potato development promotes the transformation of C-type (mixed A- and B-type) starch polymorphic structure to pure A-type.[4–6] This can also be achieved by heat–moisture regimes in vitro. Heating

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of starch–moisture systems with a low or middle moisture content at a temperature >100 °C often results in transformation of the less thermodynamically stable B-polymorphic structure (with hexagonal packing of double helices and about 36 water molecules inside every cell) to a more stable monoclinic structure of A-type polymorphs (with about six water molecules inside the helices), as has been described elsewhere.[7–11] In starches with complex A- and B-type mixtures, such heating can modify the proportion of A- and B-polymorphs in starch crystalline structure. Some authors have also postulated similar effects during annealing,[12–14] but this is disputed.[11] It has been suggested that starch structural transformations induced by increased growth temperature are similar to modifications induced by annealing.[15,16]

Starches extracted from sweet potato tubers (*Ayamurasaki* and *Sunnyred*) grown under different soil temperature regimes[17] provide an excellent opportunity to compare and contrast crystalline characteristics generated in a mixed polymorphic system. This is the focus of the present study.

2. Materials and methods

2.1. Materials

Native starch samples were obtained as follows: Orange-fleshed sweet potato cultivars *Sunnyred* and purple-fleshed *Ayamurasaki* were grown in a temperature-controlled greenhouse at the Kyushu National Agricultural Experiment Station at Miyakonojo, Miyazaki, Japan. All details about sweet potatoe growth, starch isolation and the general characteristics of the isolated starches have been reported elsewhere.[17]

2.2. Annealing procedure

Aqueous dispersions of native starch (0.3%, 10 mL) in tightly closed tubes were incubated in thermostatic cells at desired temperatures/times (Table 1). The dispersions were re-suspended every 0.5 h by gently shaking. The temperatures of annealing were chosen to be 2–3 K below the onset melting temperature of native starches. For preparation of the annealed starches dispersions in 0.6 M KCl, half of the aqueous dispersions of annealed starch after the desired incubation period were separated and centrifugated (1500 × g, 10 min) for phase separation, whereupon the supernatant was discarded, and the solid residues were air dried at 25 °C for 24 h. After that 5 mL of 0.6 M KCl solution was added.

2.3. High-sensitivity differential scanning calorimetry (HSDSC)

High-sensitivity differential scanning calorimetry (HSDSC) measurements of 0.3% aq or salt (0.6 M KCl) dispersions of starch were performed using a DASM-4 microcalorimeter (Moscow, Russia) in 0.5-cm^3 cells. Distilled water or 0.6 M KCl solution was used as a reference material. The cells were sealed and heated from 20 to 120 °C at 2 °C min^{-1} at 2.5 bar.

2.4. Calculations

The gelatinisation (melting) peak temperature (T_m) as well as gelatinisation (melting) enthalpy (ΔH_m) was determined from the HSDSC endotherms. Each sample was run in at least in duplicate, and the averaged values were used. Standard deviations were: ±0.5 K for T_m and

Table 1. Melting characteristics for aqueous suspensions of starches extracted from sweet potato *Ayamurasaki* and *Sunnyred* varieties grown at different temperatures

Annealing duration (h)	T_m (K)	ΔT^*	ΔH_m (J/g starch)	ΔH^{vH} (J/g starch)	v, anhydroglucose units	L (nm)
*Ayamurasaki—15***						
0	330.0	33.3	14.5	164.0	11.7	4.10
1	332.9	23.8	16.2	209.8	12.9	4.52
4	336.2	19.7	15.3	275.0	17.9	6.27
8	336.9	19.9	14.5	275.0	18.9	6.63
*Sunnyred—15***						
0	328.3	29.0	16.8	202.6	12.0	4.20
1	332.3	20.0	15.2	228.6	15.0	4.25
4	335.0	15.7	14.6	249.4	17.0	6.00
10	336.0	16.0	14.1	259.1	18.5	6.45
*Sunnyred—33***						
0	351.5	13.5	17.1	303.0	17.5	6.13
1	353.0	11.9	19.7	353.5	17.9	6.25
4	354.0	11.5	19.1	353.3	18.5	6.53
10	354.7	12.0	18.2	370.12	20.4	7.15

Notes: *ΔT is difference between onset temperature and final temperature of melting ($T_c - T_o$).

**Numbers correspond to soil temperature at which these varieties were grown.

±0.3 kJ mol^{-1} for ΔH_m. The value of 162 g mol^{-1} was used for converting the thermodynamic parameters per mol of anhydroglucose unit.

The values of the van't Hoff enthalpy (ΔH^{vH}) were determined according to previously described methods.[18]

The melting of the cooperative units (v) and the thickness of crystalline lamellae ($L_{crl.}$) were calculated according to[18–20] from Eqs. 1 and 2, respectively, as:

$$v = \Delta H^{vH} / \Delta H_m \quad (1)$$

where ΔH_m is the experimental melting enthalpy of starches. The standard deviation for v was about 1.2 units.

$$L_{crl.} = 0.35v \quad (2)$$

where 0.35 nm is, according to Ref. 21, the pitch height per anhydroglucose residue in a double helix.

2.5. Deconvolution procedure

A peak fit program (Gandel Scientific software) was used for deconvolution of the complex shaped DSC endotherms obtained for starch melting in 0.6 M KCl.

3. Results and discussion

Annealing of all starches in excess of water resulted in increasing peak melting temperature (Table 1) as previously reported for starches extracted from other plants.[14–16,23–30] The most significant increment of the melting temperature value was observed after the first hour of heating. After that, increments were much lower tending at eight hours towards constant values for each starch sample. The maximal increment of melting temperature ΔT_m^{max} (the difference between peak melting temperature for native starch and for long-time annealed one) was roughly similar for both varieties of sweet potato when grown at 15 °C ($\Delta T_m^{max} = 6.9$ and 7.7 K, respectively, 7.3 ± 0.4 K on average). However, for the starch extracted from *Sunnyred* grown at 33 °C, this increment was only 3.2 K. Annealing not only shifted the peak melting temperature (higher) but also induced a sharper distribution of the DSC endotherm (Table 1). It is believed that the rise of melting temperature, as well as the narrowing of the melting peak, is related to enhancement of crystalline order.[5,11,15,16,27,29–32] It would be expected a priori that the extent of modification during annealing is dependent on initial properties of starch structure. Hence, better ordered starch structures formed at high soil temperature will be less subject to the effect of annealing compared to less ordered structures corresponding to starches formed at low soil temperatures.[5,6,29,31,32] In fact the melting temperatures for the starches extracted from *Sunnyred* grown at 15 and 33 °C, followed by annealing for 8–10 h, differed from each other by 18.7 K compared to 23.2 K for the native starches (Table 1). The DSC endotherm 'sharpening' ($T_c - T_o$) postannealing was more significant for starches grown at 15 °C compared to starches grown at 33 °C. Overall, the annealing process enhanced order in less perfect starch structures (formed at low soil temperatures) leading to structural similarity with the starches grown at the higher temperatures (Table 1).

One of the main structural characteristics of crystalline structure is the thickness of crystalline lamellae. In some native starches, this parameter reflects different growth temperature experiences (Table 1).[6,31,32] Annealing of all starches studied here results in increase of crystalline lamellae thickness. The increment of this parameter is also more essential for the starches grown at low soil temperatures (Table 1). It may be noted that the enhancement of crystalline lamellae thickness due to annealing has been observed recently for potato starches (pure B-type crystalline structure), but that enhancement was only significant for short annealing times (1 h).[29] It is believed that an increase of crystalline lamellae thickness is associated with slight elongation of pre-existing double helices due to early uncoiled ends of amylopectin chains, improvement of their registration or/and appearance of new double helices and with enhancement of amount of ordered structures.[11,15,16,27,30] It is logical to surmise that all these improvements more extensively affect structures with most structural defects or disorder. The crystalline structure of native starches corresponding to high growth temperature is initially more perfect and provides less possibilities for additional ordering (accompanied by increase of crystalline lamellae thickness). As a result, for all starches investigated, the crystalline lamellae thickness after long-term annealing become similar. This provides additional strength to the conclusion that annealing promotes structural similarity of starches from the same botanical origin, but grown at different temperatures. The average value of the crystalline lamellae thickness obtained for the annealed starches studied here (6.8 ± 0.4 nm) was equal to that suggested by Cameron and Donald for starch structure (6.65 nm).[22]

Before a more detailed discussion concerning the main factors responsible for starch melting characteristics is undertaken, the question about the identity/differences and constancy/variability of the polymorph types has to be considered. Previously it has been demonstrated[5,6] that sweet potato starch grown at high-growth temperatures (33 °C) has a pure A-type polymorphic structure, whereas low-growth temperature counterparts (15 °C) contain both A- and B-type packing of amylopectin double helices (C-type structure). Examination of possible structural changes due to annealing of the starches by DSC was performed in 0.6 M KCl. It is known that in this medium the melting temperatures of A- and B-polymorphs shift differently to higher temperatures compared to aqueous dispersions.[33,34] The DSC-traces obtained in 0.6 M KCl for annealed *Sunnyred* starch grown at 33 °C (Fig. 1) is typical of the A-type polymorph. Hence, the crystalline structure for this starch remains unchanged during annealing. For all starches extracted from sweet potatoes grown at 15 °C (native and annealed), double-peak endotherms were observed in KCl (Fig. 2), which is characteristic of the complex C-type (A+B) polymorphic structure of crystalline lamellae.[33,34] A deconvolution procedure was applied to this system, and a discrete melting temperature for each peak was obtained[5,6,29,33,34] as shown in Figure 2. The ratio of underlying areas of these two peaks reflects the ratio of full energies of the endothermic transition ($\Delta H^{\mathrm{f}}, J$) corresponding to all polymorphs. This ratio of full energies is the product of two coefficients, one of which represents the ratio of specific melting enthalpy (ΔH_{m}, J mol^{-1} glucose unit) and another is the A/B proportion (percentage) of crystalline structures with A- and B-type of packing (Eq. 3)

$$\Delta H^{\mathrm{f}}_{\mathrm{A}}/\Delta H^{\mathrm{f}}_{\mathrm{B}} = (\Delta H^{\mathrm{A}}_{\mathrm{m}}/H^{\mathrm{B}}_{\mathrm{m}}) \times \mathrm{A}/\mathrm{B} \qquad (3)$$

The specific melting enthalpies for A ($\Delta H^{\mathrm{A}}_{\mathrm{m}}$) and for B ($\Delta H^{\mathrm{B}}_{\mathrm{m}}$) starch polymorphic structures may not be equal. Nevertheless, there is good reason to consider the first ratio in Eq. 3 ($\Delta H^{\mathrm{A}}_{\mathrm{m}}/\Delta H^{\mathrm{B}}_{\mathrm{m}}$) slightly differing from the unit equation. According to X-ray examination,[5,6] native starches extracted from sweet potatoes grown at four environmental temperatures (15, 21, 27 and 33 °C) have different types of crystalline structure. Accordingly, pure A-type for the samples corresponding to high temperatures (27, 33 °C), A-type with negligible amounts of B-type polymorphs (21 °C) and C-type with a high portion of B-type at low soil temperature (15 °C). The melting of all these starches is characterised by little variation in melting enthalpy, ΔH_{m}, calculated on anhydroglucose basis (Refs. 4–6 and Table 1) regardless of crystalline type. Analogous similarities of ΔH_{m} for other A- (waxy maize and waxy barley) or B-type (amylopectin potato) structures have been described elsewhere.[35] The authors[34] also have taken into account the small differences in specific enthalpies for A- and B-polymorphs in excess KCl.

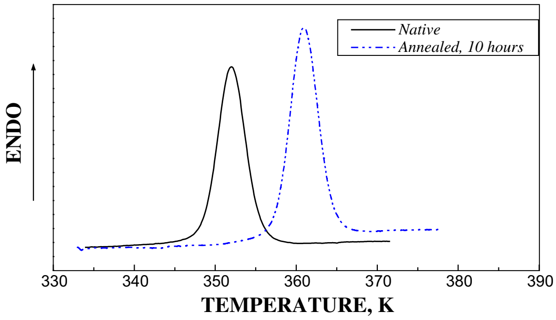

Figure 1. DSC endotherms in 0.6 M KCl for native and annealed sweet potato (*Sunnyred*) starches grown at 33 °C.

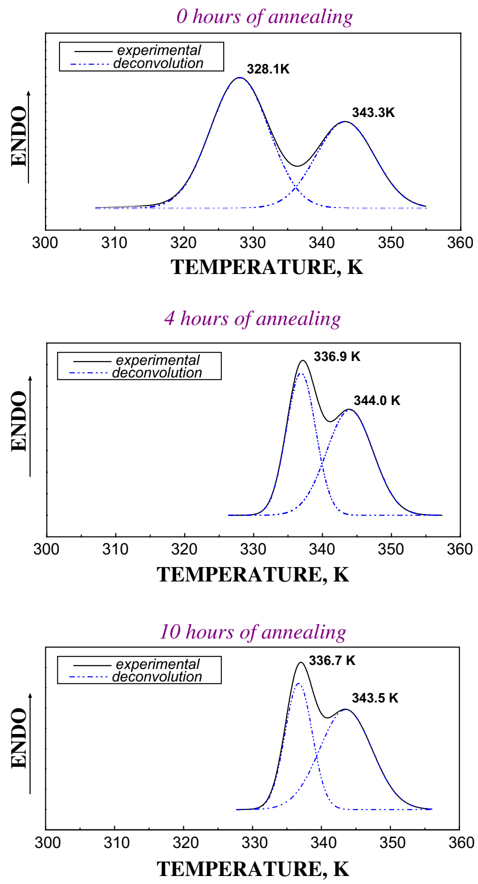

Figure 2. DSC endotherms in 0.6 M KCl for native and annealed sweet potato starches (*Sunnyred*) grown at 15 °C: experimental and deconvolution curves.

It is apparent from the data in Table 1 that, for each sweet potato starch investigated, the melting enthalpy ΔH_{m} is similar during annealing (2.5 ± 0.3 and 3.0 ± 0.2 kJ mol^{-1} for starches grown at 15 or 33 °C, respectively). All the previous text provides a basis to consider the ratio of specific enthalpies $\Delta H^{\mathrm{A}}_{\mathrm{m}}/\Delta H^{\mathrm{B}}_{\mathrm{m}}$ for two polymorphs (A- and B-type) as approximately constant and to conclude that the changes of the ratios $\Delta H^{\mathrm{f}}_{\mathrm{A}}/\Delta H^{\mathrm{f}}_{\mathrm{B}}$ (Table 2) reflect variations in proportions of A- and B-polymorphs (A/B) due to annealing. As can be seen from the data presented in Table 2, the ratio A:B rises from the value of about 35:65 (percent) for both native starches (from *Ayamurasaki* and from *Sunnyred*) formed at 15 °C to about 60:40 for annealed samples.

The annealing data (Table 2) show that starches extracted from the two sweet potato varieties grown at 15 °C, and characterised by C-type crystalline structure, may be transformed (at least, partially) from the relatively labile B-type polymorph to the more stable A-type. The A:B-ratio of the two polymorphs varies as a

Table 2. Gelatinisation temperatures in 0.6 M KCl for A- and B-polymorphs and their proportions in sweet potato starches grown at 15 °C (soil temperature)

Annealing duration (h)	T_m (K)		ΔT^*	%**		r^{***}
	A	B		A	B	
Ayamurasaki						
0	342.7	329.7	13	31.6	68.4	0.997
0****	342.2	330.7	11.5	35.4	64.6	0.988
1	342.9	334.4	8.5	44.2	55.7	0.996
4	342.5	338.0	4.5	58.5	41.5	0.999
8	342.3	338.4	3.9	58.0	42.0	0.998
Sunnyred						
0	343.2	328.1	15	39.5	59.7	0.975
4	344.0	336.9	7.1	54.0	46.0	0.995
8	343.5	336.7	6.8	60.3	40.7	0.997

Notes: *Difference between melting temperatures for A- and B-polymorphous structures.

**Relative portions of each polymorphs, evaluated by deconvolution of experimental melting curves.

***Regression coefficient for deconvolution procedure.

****Rate of heating during DSC analysis is 1 K min^{-1}.

function of annealing conditions and more especially the duration of annealing (Table 2, Fig. 2). The transformation of B- to A-type structure develops gradually during annealing up to 8–10 h, whereupon the A:B proportion reaches a maximal ratio of 60:40 (Table 2). So, the annealing process significantly changes the ratio of polymorphs due to a decrease of B-type crystallinity (and vice versa for A-type) that is analogous to environmental influence.[4–6] However, a complete conversion of C- to A-type does not take place during annealing unlike environmentally induced modification.[4–6]

As previously mentioned, the double endotherm for starches with C-type polymorphic structure (in 0.6 M KCl) corresponds to one peak representing melting of B-type polymorphs (shifted to higher temperatures in KCl in comparison with water) with another related to melting of A-type polymorphs (shifted only slightly in KCl). These data concur with data reported by other authors.[33,34] This effect is obvious for native starches grown in this study at 15 °C where the difference in peak melting temperature in 0.6 M KCl for the A- and B-forms is 12–13 °C (Table 2). For annealed starches in water, the single endotherm shifts to a higher temperature, whilst in KCl only the melting temperature of the B-type polymorph is increased (Fig. 2, Table 2). During long-term annealing the A- and B-type polymorph peaks progressively overlap, whereby in KCl they becomes less and less distinct (ΔT_m equals 4 or 7 °C after eight hours annealing versus 13 or 18 °C for native starch from *Ayamurasaki* and *Sunnyred*, respectively).

There is another aspect that must be examined, taking into account the structural modification during annealing. According to the data generated here, even short heating of starch suspensions results in partial B- to A-type polymorph transformation and accordingly changes of their relative proportions (Table 2). Theoretically, this structural transformation may occur (to some degree) during DSC analysis. For verification of such a possibility, DSC analysis of native *Ayamurasaki* starch grown at 15 °C was conducted in KCl at a heating rate of 1 K min^{-1} (half the heating rate used throughout this study) in order to elongate the heating duration. As can be seen from Table 2, the A to B ratio is independent of DSC duration, and for the conditions used, no B to A transformation occurred during analysis.

4. Conclusions

For annealed sweet potato starches, increased gelatinisation (melting) temperature and crystalline lamellae thickness with decreased ΔT_m ($T_c - T_o$) is more pronounced for less ordered structures (formed at low soil temperatures) than for those initially characterised by more perfect crystalline structures (formed at high soil temperatures). As a result, the annealed starches reach a much more similar state with respect to crystalline structure and, accordingly, gelatinisation characteristics.

Long annealing times of starches with mixed C (A plus B)-type crystalline structure lead to partial transformation of B- to A-type polymorphs with changes in the A to B-proportions. These data differ from those obtained by environmental temperature variation during biosynthesis, which results in full conversion of C-(low growth temperature) to pure A-type (corresponding to high temperature) structure. Hence, the events regulating starch supramolecular organisation during biosynthesis have both genetic and environmental regulations, although the relative effects are not understood.

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