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Short communication

Annealing of starches from potato tubers grown at different environmental temperatures. Effect of heating duration

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Abstract

On annealing of starches extracted from potato tubers grown at different soil temperatures (10, 16, 20 and 25 °C) an increase of crystalline lamellae thickness accompanied by enhancement of melting temperature has been observed. The perfection of crystalline structure in starches during annealing most likely can be attributed to additional lengthening of double helices and to optimization of their registration within the crystalline lamellae. The first process possibly takes place at short-term heating period (1–2 h) while the second occurs at long-term heating (6–10 h). As a result of annealing starches with more similar and more perfect structures than native ones were obtained.

Keywords: Potato starches; Annealing duration; Thermodynamic melting parameters; Differential scanning calorimetrical-analysis

1. Introduction

Annealing of starch is the incubation of starch dispersions in excess of water at temperature between the glass transition temperature and onset of melting. Such starch heating causes an increase in granular stability (Hoover & Vasanthan, 1994; Marchant & Blanshard, 1978) associated with an increase of melting temperature and narrowing of the melting temperature range.

Though this phenomenon has been extensively described there is no clear agreement on mechanisms. The following main processes occurring during annealing were suggested as a possible cause of the changes in physicochemical starch characteristics: (i) structural modifications of crystalline regions, namely conversion of B- to A-polymorphs (Donovan, Lorenz, & Kulp, 1983; Knutson, 1990; Zobel, 1988a,b); (ii) changes in the amorphous region decreasing their destabilization effects on crystallites (Donovan et al., 1983; Hoover & Vasanthan, 1994; Jacobs & Delcour, 1998; Tester, Debon, & Karkalas, 1998); (iii) improvement of crystallinity and perfection of starch crystallites mainly due to formation of new crystals and recrystallization (Donovan et al., 1983) or registration of double helices (Jacobs, Eerlinger, Rouseu, Colonna, & Delcour, 1998; Knutson, 1990; Tester et al., 1998; Yost & Hoseney, 1986) or lengthening of amylopectin double helices without increasing their number (Jacobs & Delcour, 1998; Tester et al., 1998; Tester, Debon, & Sommerville, 2000).

It has been also concluded (Tester et al., 2000), that the rate of changes during annealing is dependent on the initial properties of both regions of crystalline structure. Recently it has been shown (Genkina, Noda, Koltisheva, Wasserman, Tester, & Yuryev, 2003; Protserov, Wasserman, Tester, Debon, Ezernitskaja, & Yuryev, 2002; Tester, 1997) that the crystalline characteristics are affected by environmental conditions during starch biosynthesis mostly by soil temperature, so it may be proposed a priori that the characteristics of the starches grown on soil with different temperatures will change due to annealing in a variable degree. The aim of this study is to examine this proposal on starches extracted from potatoes grown in soils with different temperatures. The differential scanning calorimetrical (DSC)-method was applied.

2. Materials and methods

2.1. Materials

Potato (cv Maris Piper) tubers were grown at the Scottish Crop Research Institute (SCRI) at the temperature-

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Table 1
The values of the melting temperatures (T_m), melting enthalpy (ΔH_m), van't Hoff enthalpy (ΔH^{vH}), melting cooperative units (ν), and the thickness (L_{crl}) of crystalline lamellae for native and annealed potato starches in water

Temperature of soil (°C)	Annealing		T_m (K)	ΔH_m (kJ mol^{-1})	ΔH^{vH} (kJ mol^{-1})	ν, anhydro-glucose units	L (nm)
	Tempe-rature (°C)	Duration (h)					
10	49	0	333.5	2.65	40.0	15.7	5.3
		1	337.3	2.29	51.8	22.6	7.9
		3	338.4	3.25	62.9	19.3	6.8
		7	339.5	3.73	71.1	19.1	6.6
		10	339.7	3.95	75.0	19.0	6.6
		10	340.3[a]				
16	50	0	336.0	3.54	50.0	14.2	5.1
		1	339.7	3.64	66.9	24.7	8.6
		3	340.5	3.97	72.2	18.2	6.4
		7	341.4	3.39	66.8	19.7	6.9
		10	341.2	4.00	75.6	19.0	6.6
20	55	0	338.9	3.30	48.3	14.1	5.0
		1.5	343.0	2.37	52.3	22.1	7.7
		3.5	344.2	3.57	68.1	19.1	6.7
		7.0	345.3	3.75	72.3	19.3	6.8
		10	345.3	3.79	77.9	20.5	7.2
		10	346.0[a]				
25	59	0	343.8	4.82	53.0	12.3	4.3
		2	347.5	3.32	66.2	19.9	7.0
		4	348.2	3.85	76.8	19.9	7.0
		7	348.7	3.97	79.2	19.9	6.9
		10	349.1	4.38	82.5	18.9	6.6

[a] The values were obtained in 1.5 M solution of KCl.

controlled conditions. Detailed description of potato tuber growth, starch extraction as well as the characteristics of native starches was reported earlier (Tester, Debon, Devies, & Gidley, 1999).

Annealed starches. The aqueous dispersions of native starch (10 ml, 0.3%, w/w) in tightly closed tubes were kept in a water bath at a corresponding temperature for different times (the values are given in Table 1). The temperatures of annealing were chosen as 2–3 °C below the onset melting temperature of the native starches.

2.2. DSC-study

DSC measurements of 0.3% aqueous or salt (1.5 M KCl) starch dispersions were performed using high-sensitive microcalorimeter DASM-4 (Russia) in 0.5 cm^3 cells. Distilled water or 1.5 M KCl solution was used as reference material. The cells were sealed and heated from 20 to 120 °C at a heating rate of 2° min^{-1} and 2.5 bar excess pressure.

2.3. Calculations

The melting peak temperature (T_m) as well as melting enthalpy (ΔH_m) was determined from the DSC-endotherms. Each sample was run in triplicate. Standard deviations were ± 0.5 K for T_m and ± 0.3 kJ/mol for ΔH_m. The value of 162 g mol^{-1} was used for calculating the thermodynamic parameters per mol of anhydroglucose unit.

The values of van't Hoff enthalpy (ΔH^{vH}) were determined accordingly to paper (Matveev et al., 2001).

The calculations of melting cooperative unit (ν) and the thickness of crystalline lamellae (L_{crl}) were described early (Kiseleva, Tester, Wasserman, Krivandin, Popov, & Yuryev, 2003; Protserov et al., 2002).

Eq. (1) (Thomson-Gibbs' relationship) and the Eqs. (2) and (3) allowed the free surface energy (γ_i), surface enthalpy (q_i) and entropy for the face side of the crystalline lamellae (s_i) to be evaluated (Kiseleva et al., 2003; Protserov et al., 2002):

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

where T_m^0 and ΔH_m^0 are the melting temperature and the melting enthalpy of a hypothetical crystal with unlimited size (a perfect crystal), ρ_{crl} and L_{crl} are the density and the thickness of the crystal, respectively.

$$q_i = [(\Delta H_m^0 - \Delta H_{exp})\rho_{crl} L_{crl}]/2.5 \quad (2)$$

$$\gamma_i = q_i - T_m s_i \quad (3)$$

Since the values of T_m^0 and ΔH_m^0 for a perfect crystal are not available, for calculations of the surface thermodynamic parameters the values of the T_m^0 (346.8 K) and the ΔH_m (35.5 J g^{-1}) for B-type spherolitic crystals were used, as well as values of ρ_{crl} for B-type structures (1.4 g cm^{-3}) (Tester, 1997; Whittam et al., 1990).

3. Results and discussion

The conditions of annealing (temperature and duration) as well as some characteristics obtained from DSC-thermograms and calculated from appropriate equations are listed in Table 1. The low starch concentration used as well as low heating rate allows a quasi-equilibrium approach to be applied (Bogracheva, Wang, Wang, & Hedley, 2002). It can be seen that the melting temperature increases at annealing for all starch samples investigated as has been previously observed for starches from different plants (Jacobs & Delcour, 1998; Kiseleva et al., 2003; Protserov et al., 2002; Tester et al., 2000). This increase occurs only in the first 1–2 h of heating whereas after 8–10 h of heating these melting parameters reach their maximum values for all starches. For changes of starch melting enthalpy the following tendency was observed: after first 1–2 h of heating it decreases and than at longer times slowly increases exceeding the initial magnitude (low soil temperature) or equaling it (higher soil temperature). All starches annealed during 10 h are characterized by similar values of the melting enthalpy (4.03 ± 0.30 kJ mol^{-1}).

According to the Thomson-Gibbs' Eq. (1) (Bershtein & Egorov, 1994), the change of melting temperature of semi-crystalline synthetic polymers can be described as a function of three following variables: the thickness of crystalline lamellae ($L_{crl.}$), the free surface energy of face side of crystals (γ_i) and its polymorphous structure. Since starch has a semi-crystalline polymeric structure the application of this equation for the description of the starch melting process is acceptable.

The initial thickness of crystalline lamellae equal to about (4.9 ± 0.5 nm) for all native starches (Protserov et al., 2002; Table 1). Analysis of data obtained for annealed starches (Table 1) shows that annealing leads to an increasing of crystalline lamellae thickness, which becomes equal to 6.8 ± 0.3 nm after a long annealing (10 h) of all starches. The maximal enhancement of this parameter has been noticed after a brief annealing (1–2 h): the average value was of 7.8 ± 0.8 nm, followed by slight decrease after further heating. This effect could be caused by formation at the first annealing stage of some energetically unstable state of crystalline lamellae which has then been improved.

Generally, as a result of annealing the average value of the crystalline lamellas thickness after annealing exceeds the initial one for native starches at about 50% (Table 1). The increase of the crystalline lamellas thickness may be caused by a formation of new double helices and/or a lengthening of double helixes pre-existing in native starches. The increment of melting temperatures on annealing can be, at least partially, a result of these processes.

To ascertain the nature of all processes resulted the increase of melting temperature at annealing of the starches investigated the possible changes in polymorphic structure have been studied. Zobel (1988a, 1988b) and Knutson (1990) postulated the probability of conversation of B- to A-conformation during annealing. According to well known and at present the conventional method (Bogracheva, Morris, Ring, & Hedley, 1998), the simple way to verify the type of starch polymorphous structure is carrying out the comparative calorimetric experiments with starch suspension in water and in solutions of KCl. In this salt medium the melting temperature of B-type polymorphous structure increases by 1–3 °C compared to pure water, while the A-polymorph causes an increase of 7–12 °C (Bogracheva et al., 1998; 2002). The data obtained for annealed starches due to such experiments (Table 1) are typical for pure B-polymorph but not for the A or C-type. So the annealed starches as well as native ones have a B-type polymorphic structure and no changes in the structural type of potato starches takes place even after a long annealing.

Another factor that could affect the starch melting temperature is the surface entropy of crystalline lamellae which makes the main contribution to the magnitude of the surface energy in the Thomson-Gibbs' relationship and is proportional to the amount of defects in the structural organization of the starch granules (Bershtein & Egorov, 1994; Protserov et al., 2002). Some enhancement of the surface entropy values for all short annealed starches (Table 2, 1 h of heating) confirms the assumption about the formation of the energetically unstable state in the crystalline region of the potato starch granule in the first stage of heating. At the same time, the data obtained does not allow a precise conclusion about the influence of annealing on the amount of defects in the starch crystalline structure.

All the results obtained can be summarized as follows: (a) the short-time and long-time annealing of all the starches

Table 2
The values of free energy (γ_i), enthalpy (q_i) and entropy (s_i) of the surface of face side for crystals of native and annealing potato starch

Temperature of soil (°C)	Annealing		$\gamma_i \times 10^7$ (J cm^{-2})	$q_i \times 10^7$ (J cm^{-2})	$s_i \times 10^7$ (J cm^{-2} × grad^{-1})
	Temperature (°C)	Duration (h)			
10	49	0	5.0	56.7	0.15
		1	5.3	94.8	0.26
		3	3.4	58.7	0.16
		7	3.5	46.7	0.13
		10	3.3	41.5	0.11
16	50	0	3.4	41.6	0.11
		1	4.3	60.7	0.17
		3	2.8	46.4	0.13
		7	2.7	56.0	0.16
		10	2.6	40.7	0.11
20	55	0	2.6	41.9	0.12
		1.5	3.8	90.3	0.25
		3.5	1.2	50.2	0.14
		7.0	0.73	46.7	0.13
		10	0.68	40.7	0.12

extracted from the potato grown at different environmental temperatures causes different changes in their physico-chemical parameters; (b) during the first 1–2 h of heating the melting enthalpies diminish while the thickness of the crystalline lamellae increase; (c) the longer heating causes a rise of melting enthalpies, some decrease of the thickness of crystalline lamellae and perhaps a small reduction in the entropic factor; (d) all these characteristics become about the equal for all annealed starches after long heating; (e) these changes are accompanied by an increase in melting temperature.

4. Conclusions

The rising of melting temperature during annealing of all starches extracted from the potato grown at different environmental temperature is a result of increasing crystalline structure perfection. Two processes certainly contribute to this perfection: the lengthening of amylopectin pre-existing double helices caused by their additional completeness due to initially uncoiled ends and the improvement of their registration. During the first 1–2 h of heating the former process plays the more important role whereas more prolonged heating (>4 h) initiates the second process as the main one. The most elevation of melting temperature occurs during the shot-time period of annealing so this elevation is in the most part affected by the process of expansion of double helices. As a result of a long heating time the annealed starches were obtained with about equal structural characteristics, such as the melting enthalpy and the thickness of crystalline lamellae, independently of initial structural perfection for these starches.

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