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Differential scanning calorimetry and a model calculation of starches annealed at 20 and 50 °C

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Abstract

Corn, wheat, and potato starches were annealed at 20 and 50 °C, and the gelatinization phenomena were observed with differential scanning calorimetry (DSC). Amylose content and amylopectin chain length distribution were not changed by the annealing treatment. The DSC endotherm associated with gelatinization of amylopectin shifted to a higher temperature, and became narrower and deeper after annealing at 50 °C; however the conclusion temperature and enthalpy of gelatinization were similar. The ordered structures of amylopectin, formed by a varying number of links by hydrogen bonds, were cleft at the gelatinization temperature. Model calculation suggested that more links (N) would be generated in each ordered amylopectin region, and the number of ordered regions (M) would be reduced by annealing at a higher temperature. However, the total number of links in amylopectin, represented by the product ($N \times M$), was similar for cereal starches and only slightly increased for potato starch.

Keywords: Starch; Annealing; Amylopectin; Differential scanning calorimetry (DSC); Gelatinization

1. Introduction

Starch consists of two glucans, which are essentially linear amylose and highly branched amylopectin (Blanshard, 1987), and is a partially crystallized structure as observed by X-ray diffraction (Biliaderis, 1990). The crystalline structures are formed by hydrogen bonds, and the cluster model is widely accepted for the ordered structures in starch (Hizukuri, 1986).

The molecular structure of starch differs by botanical source. Cereal starches like corn and wheat have an A-type crystal, while a tuber starch such as potato exhibits a B-type crystal in its X-ray diffraction pattern (Biliaderis, 1991; Hizukuri, 1985). The size of one cluster in starch was estimated by means of X-ray diffraction. Both polymorphs are composed of ordered arrays of double helices made up of two parallel single strands (Imberty, Chanzy, Pérez, Buléon & Tran, 1988; Imberty & Pérez, 1988). The A-type crystal is a closely packed arrangement of double helices, while the B-type structure is more open with more interhelical water (Biliaderis, 1991; Gernat, Radosta, Anger & Damaschun, 1993; Gidley, 1987). The A-type crystal is more stable in terms of thermodynamics, while the B-type is the kinetically favored polymorph (Gidley & Bulpin, 1987; Knutson, 1990). Growth temperature also influences starch structures because it may change the ratio of amylose and amylopectin, the molecular structure of both components, and the amylopectin chain length distributions (Gernat et al., 1993; Gidley, 1987; Gidley & Bulpin, 1987; Tester & Karkalas, 2001).

When starch is heated in the presence of enough water, its crystalline organization decomposes to form amorphous regions (Atwell, Hood, Lineback, Varriano-Marston & Zobel, 1988). This molecular disordering is called gelatinization and is a frequently observed endothermic phenomenon using differential scanning calorimetry (DSC) (Biliaderis, 1990; 1991). The endothermic peak associated with gelatinization originates from the amylopectin. As the endothermic peak area appearing near the gelatinization temperature generally correlates with amylopectin content (Russell, 1987), loss of the ordered structure, i.e. the double helices, in amylopectin can be quantified by the heating DSC measurement.

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Starch is annealed when heated for several hours with excess water at a temperature between the glass transition and the onset of gelatinization temperatures (Stute, 1992; Tester & Debon, 2000). Annealing is a physical reorganization that exhibits an observable increase in gelatinization temperature and a narrowing of the range between the onset and conclusion temperatures (Tester, Debon & Karkalas, 1998). Gough and Pybus (1971) treated wheat starch in water at 50 °C for 72 h and observed higher gelatinization temperature with much narrower range, based on loss of birefringence. The same temperature was adopted by a number of researchers for corn (Krueger, Knutson, Inglett, & Walker, 1987), wheat (Hoover & Vasanthan, 1994; Jacobs, Eerlingen, Clauwaert, & Delcour, 1995), and potato (Hoover & Vasanthan, 1994; Jacobs et al., 1995; Muhrbeck & Svensson, 1996). This is because 50 °C is slightly below the gelatinization temperature, at which the annealing effect of elevating gelatinization temperatures is markedly apparent (Knutson, 1990; Krueger et al., 1987; Tester et al., 1998). Annealing could be initiated in wheat starch that contained more than 20% w/w moisture, but it was restricted to a water content lower than 60% w/w (Tester et al., 1998). As a physical process, annealing did not influence the amylose and amylopectin ratio or the amylopectin chain-length distributions, but the ordered structures developed a more stable form with a smaller dispersion than those in the original starch. According to Tester et al. (1998), annealing improves the ordered structure in starch by increasing the number of links, but the number of crystalline regions in starch does not change. Annealing may occur during commercial starch processing because the temperature and moisture conditions are similar to wet milling (Krueger et al., 1987; Tester & Debon, 2000). There have been numerous recent studies on starch annealing (Hoover & Vasanthan, 1994; Jacobs et al., 1995; Krueger et al., 1987; Muhrbeck & Svensson, 1996; Stute, 1992; Tester et al., 1998; Tester & Debon, 2000), but most of them dealt with the phenomenological aspect. Little theoretical evidence has been presented for annealing effects on ordered structures in starch.

DSC gelatinization curves and the structure of the ordered region in amylopectin were examined using the zipper model presented by Nishinari, Koide, Williams and Phillips (1990). The zipper model was also used to explain the endothermic peaks in DSC curves for the gel–sol transition of thermo-reversible gels. Most gels consist of a somewhat crystalline region, called the junction zone, usually considered to be an association of rod-like or helical molecules, and a somewhat amorphous region. The DSC peaks that accompany a gel–sol transition result from melting of the crystalline region. As a model for the structure of the crystalline region, molecular zippers are used to represent rigidly ordered molecular structures, such as helices or extended molecules. The disappearance of the crystalline region is equated with the opening process of the molecular zippers. The molecular forces that cause these helices or rods to aggregate are generally believed to be secondary forces, such as hydrogen bonds.

The ordered structure of starch is known to be composed of double helices (Imberty et al., 1988; Imberty & Pérez, 1988), which may not be completely similar to that of polysaccharide gels. Such a gel is formed not only by hydrogen bondings but also by ionic and van der Waals interactions, and may contain single or double helices, and melts thermo-reversibly. However, the zipper model is versatile and can be applied to any structure in which the links forming the ordered region open one by one. Gelatinization of starch involves a process that hydrogen bondings making the ordered region of amylopectin cleave. Therefore, the zipper model can be useful to analyze the gelatinization observed in a heating DSC curve, although the structure of the ordered region may not be like a zipper. The zipper model was first applied to the gelatinization of starch by Kohyama and Nishinari (1991). In this study, we obtained a good fit with gelatinization of corn, wheat, and potato starch samples annealed at 20 and 50 °C. The structure of crystalline regions in amylopectin became highly homogeneous after annealing. Using the best-fit parameters, we discuss the structures of the ordered region in amylopectin.

2. Materials and methods

2.1. Starch

Chemical grades of wheat, corn, and potato starches (Wako Chemical Co., Tokyo) were purchased. As their growth environment and processing temperature were unknown, we chose two annealing temperatures (20 and 50 °C). The former is close to environmental temperature and the latter was used in many previous studies (Gough & Pybus, 1971; Hoover & Vasanthan, 1994; Jacobs et al., 1995; Krueger et al., 1987; Muhrbeck & Svensson, 1996). The original starches exhibited gelatinization temperatures above 50 °C. Starch samples were annealed by keeping the mixture of starch and water (1:10) in a water bath (either of 20 or 50 °C) for 72 h. After centrifugation, the precipitate was dried over diphosphorus pentaoxide. Annealed starches were then stored for 10 days in a desiccator containing saturated magnesium nitrate. The relative humidity of 0.52 produced starch samples with a constant water content of 14.0% w/w.

Amylose content was determined by the method developed by Gibson, Solah and MacCleary (1997) using an amylopectin-amylose assay kit (Megazyme International Ireland Ltd, Ireland). The distribution of amylopectin chain lengths was determined by high-performance anion exchange chromatography after debranching by isoamylase (Katayama, Komae, Kohyama, Kato, Tamiya and Komaki, 2002; Nagamine & Komae 1996). Each sample was analyzed twice.

2.2. Differential scanning calorimetry

DSC measurements were performed using an SSC5200H system with a DSC120 module (Seiko Instruments Inc., Tokyo). Starch (2.5 mg) and distilled water (47.5 mg) were weighed directly in a 70 μL silver pan, and the pan was sealed hermetically. A pan containing 48 mg of water was used as a reference. The pans were heated from 25 to 130 °C at a rate of 0.0167 °C/s. The slow heating rate (1.0 °C/min) was chosen to fit the DSC data with calculated curves as shown below. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), enthalpy of gelatinization (ΔH), peak width at half height (W_d), and peak height (H_p) of each observed curve were determined (Kohyama, Matsuki, Yasui & Sasaki, 2004). Each sample was measured triplicate. These DSC parameters per starch weight were less dependent on the starch concentration when the concentration was less than 10% w/w (Biliaderis, 1990; Kohyama & Nishinari, 1991).

2.3. Zipper model analysis

We analyzed the DSC curves using the zipper model (Nishinari et al., 1990). Each molecular zipper consists of N parallel links that can be opened from both ends. When the links 1, 2,…, p are all open, the energy required to open link $p+1$ is assumed to be E. It is assumed that each open link can assume G orientations: i.e. the open state of a link is G-fold degenerate, which corresponds to the rotational freedom of a link. According to this treatment, the heat capacity C of such a system consisting of M zippers can be written as

$$C = M\{\log(G/x)\}^2[2x/(1-x)^2 + N(N+1)x^N \times\{-x^{N+1} + (N+1)x - N\}/\{1-(N+1)x^N + Nx^{N+1}\}^2]$$

where $x = G\exp(-E/kT)$, in which E represents the energy required to open the link, k is the Boltzmann constant (1.38×10^{-23} J K^{-1}), and T is the absolute temperature.

Curves calculated using various parameters (E, N, G, and M) in the zipper model were fit to the observed DSC curves. The calculation was based on two assumptions (Kohyama & Nishinari, 1991). First, it was assumed that only one kind of zipper or ordered region existed in the system to avoid complicated calculations and to determine a unique parameter set. However, it should be noted that starch is polydisperse; i.e. many kinds of ordered regions are possible in the system and may show various distributions of the parameters. Although the ordered structure of amylopectin may not be unique, the variation becomes much smaller after annealing. Second, heating at a slow rate of 1.0 °C/min was considered an equilibrium state, since the model is based on statistical mechanics. We confirmed that when a slower heating rate (<1.0 °C/min) was used, little difference was observed in heating DSC curves for the various types of measurements. For example, only a 0.2 °C difference was seen in T_p.

3. Results and discussion

3.1. Chemical structure of starch

Table 1 shows amylose content and the chain length distribution of amylopectin. All the starches annealed at 20 and 50 °C exhibited similar amylose content and close distribution of chain length in amylopectin (Fig. 1). The amylose content and chain length distribution have similar characteristics as reported in previous studies (Hizukuri, 1985; Koizumi, Fukuda & Hizukuri, 1991; Nagamine & Komae, 1996). Corn starch treated at 50 °C exhibited a significantly greater percentage of short chains (DP 6–12) and significantly smaller middle chains (DP 13–24 and DP 25–35) in amylopectin than that at 20 °C (statistically examined by t-test as $p<0.05$). However, as shown in Fig. 1, both samples had very close distributions of amylopectin chain length. This seems to be due to very small variances found in the two replicates. Therefore, we conclude that the annealing was a completely physical process, where the covalent bondings included in amylopectin and amylose did not change.

3.2. Observed DSC curves

Fig. 2 depicts typical DSC curves observed in starch gelatinization. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and peak width at half

Table 1
Amylose content and chain length distribution of starch samples

Sample	Annealing temperature (°C)	Amylose content[a] (%)	DP 6-12[a] (%)	DP 13-24[a] (%)	DP 25–35[a] (%)	DP 36–[a] (%)
Wheat	20	29.20±0.08	25.2±0.3	43.2±0.4	14.2±0.0	15.1±0.6
	50	29.07±0.36	24.7±0.0	43.7±0.1	14.3±0.1	14.9±0.1
Corn	20	24.88±0.17	21.8±0.0	48.2±0.0	13.8±0.0	13.6±0.1
	50	24.73±0.03	22.6±0.0	47.8±0.0	13.5±0.0	13.5±0.1
Patoto	20	22.68±0.91	17.4±1.2	41.9±2.1	12.5±0.2	25.6±2.9
	50	22.79±0.31	15.8±0.7	40.2±1.4	12.4±0.0	28.9±2.1

[a] Mean and standard deviation values of duplicates.

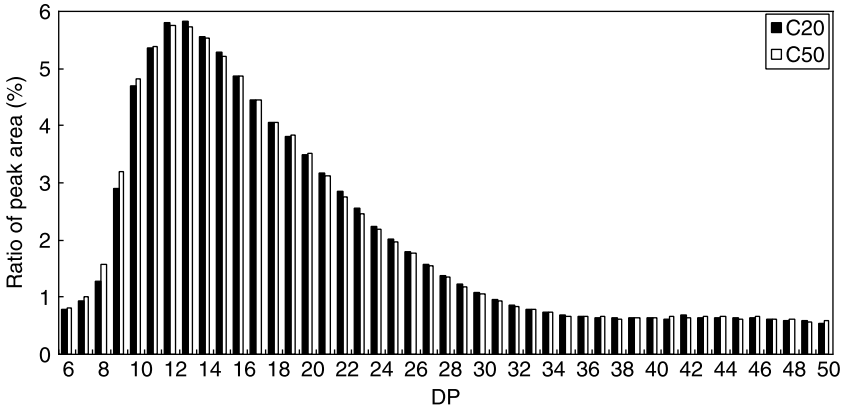

Fig. 1. Chain length distribution of corn starch samples. C20, annealed at 20 °C, and C50 annealed at 50 °C. Mean values of duplicate analysis for percentages of each degree of polymerization (DP).

height (W_d) were read directly. The peak height (H_p) was calculated from the depth of an endothermic peak.

Observed DSC curves after annealing at 20 °C were closer to those without annealing for the three starches (data not shown) than those after the 50 °C treatment. The thermal history for commercial starches was unknown, but they were likely treated at around environmental temperature. Starch samples were annealed at two different temperatures for the same period. The gelatinization peak after annealing at 50 °C was shifted to a higher temperature and became sharper, and the peak height was greater than that treated at 20 °C. These observations were consistent with previous results of annealing various starches, and the differences in gelatinization temperatures were in the range of annealing effects when compared to those without annealing treatment (Jacobs et al., 1995; Knutson, 1990; Muhrbeck & Svensson, 1996; Tester et al., 1998; Tester & Debon, 2000).

Table 2 shows DSC results. The DSC endotherm associated with gelatinization of amylopectin shifted to a higher temperature and became narrower and higher after annealing at 50 °C. In Table 2, the onset and peak temperatures of gelatinization, enthalpy, half width, and peak height of the gelatinization endotherms were increased (examined by *t*-test; $p<0.001$), while the conclusion temperature was similar ($p>0.05$). The gelatinization temperature was wheat < potato < corn for both annealing temperatures. Enthalpy for gelatinization was wheat < corn < potato, which did not directly relate to the amylose content (Table 1). Enthalpy for gelatinization of wheat starch annealed at 50 °C was slightly lower than that at 20 °C (*t*-test; $p=0.02$), which may be due to partial gelatinization. Otherwise, the gelatinization enthalpy was not changed by the annealing temperature. The difference in gelatinization temperature between 50 and 20 °C treatments varied among the different starch sources. The annealing effects were the greatest for wheat starch and less significant for corn in terms of the onset and peak temperatures.

3.3. Meanings of zipper model prameters

The ordered structures of amylopectin formed by varying numbers of links of hydrogen bonds were cleft at the gelatinization temperature. To examine the effects of the four parameters (*E*, *N*, *G*, and *M*) in the zipper model, each was varied one at a time; the resulting curves are plotted in Fig. 3. The effect of *E* is illustrated in Fig. 3(E). Increasing the *E*-value shifted the curve to a higher temperature. Since, the gelatinization peak usually appears at 50–70 °C,

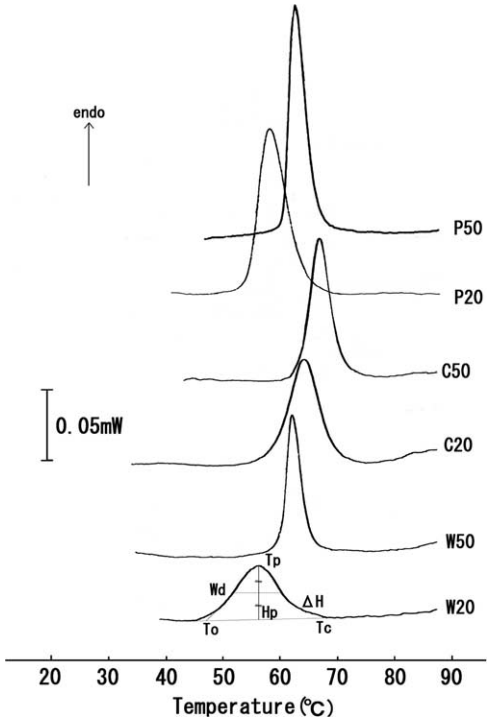

Fig. 2. Observed DSC curves for 5% w/w starch samples. Heating rate: 1.0 °C/min. Samples: wheat (W), corn (C), and potato (P) starches annealed at 20 or 50 °C. Examples of onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), peak width at half height (W_d), peak height (H_p) and enthalpy for gelatinization (ΔH) are also shown for the W20 curve. The latter two values are calculated in g-dry starch from the height and peak area of each endothermic peak.

Table 2
Characteristics of observed DSC endotherms

Sample	Annealing temperature (°C)	Observed data[a]					
		T_o (°C)	T_p (°C)	T_c (°C)	W_d (°C)	H_p (mW/g-DM[b])	ΔH (J/g-DM[b])
Wheat	20	48.2±0.4	56.2±0.2	68.5±1.2	8.67±0.15	18.2±1.4	10.6±0.3
	50	60.1±0.1	62.5±0.0	68.1±2.9	2.99±0.31	51.9±1.7	9.9±0.3
Corn	20	59.2±0.2	65.2±0.0	75.1±1.2	6.09±0.35	34.3±0.9	14.1±0.7
	50	63.1±0.1	66.7±0.2	74.7±0.9	3.88±0.17	53.7±0.2	14.2±0.4
Potato	20	54.3±0.1	58.1±0.2	70.4±0.5	5.48±0.05	51.7±0.1	19.1±0.4
	50	61.1±0.2	63.1±0.2	70.7±0.6	3.83±1.20	88.4±4.2	18.0±0.8

[a] Mean and standard deviation values of triplicates.
[b] g-Dry matter.

the *E*-value must be 2800–3000*k* (J), which corresponds to the energy of hydrogen bonds. The curve also became slightly wider with increasing *E*, but the peak height did not change. The peak shifted to a lower temperature and became higher and narrower with increasing *G*, as shown in Fig. 3(G). The temperature shift was in the opposite direction to that for annealing at a high temperature; however, the peak shape was similar to that observed after annealing. A large value of *N* gave a sharper and greater peak, but had little effect on the peak temperature, as indicated in Fig. 3(N). *N* likely increase in annealing at a higher temperature. *M* had absolutely no effect on peak temperature or the width; however, the peak height increased in proportion to *M* (Fig. 3(M)).

Therefore, the major factor in determining peak temperature is *E*, followed by *G*. Peak width is determined principally by *N*, and secondarily by *G*. Peak height is influenced by both *N* and *M*. Consequently, curve fitting for the observed DSC endotherms was performed in the following order: (1) estimation of the peak temperature by varying *E* and *G*, (2) determination of the half width at various *N*, and (3) calculation of *M* based on the observed peak height.

3.4. Calculated parameters

Table 3 presents the best-fit results for zipper model parameters (*E*, *N*, *G*, and *M*) and calculated values for the peak temperature and half width. We compared them with the mean parameters of the observed DSC curves for six samples (Table 2). The typical error between the observed values and those of the best-fit curve was <0.1 °C for T_p,

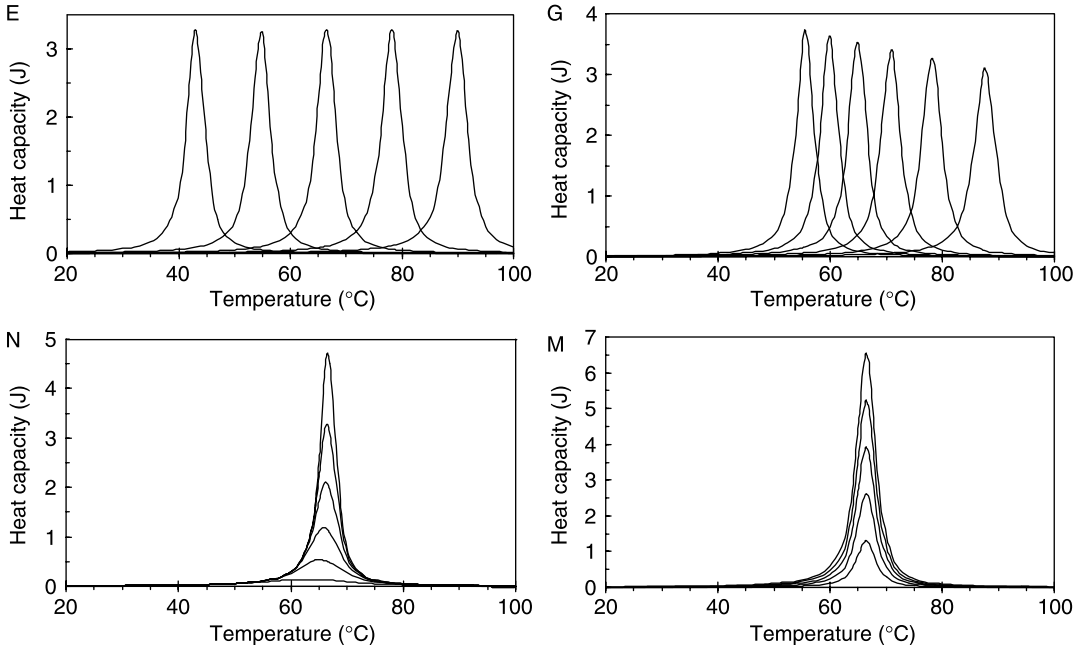

Fig. 3. Heat capacity as a function of temperature calculated by the zipper model equation while varying only one parameter. (E) Dependence of *E*. $N=100$, $G=5000$, and $M=5\times10^{18}$ are fixed. *E* is 2700*k*, 2800*k*, 2900*k*, 3000*k*, and 3100*k* (from left to right). (G) Dependence of *G*. $E=3000k$, $N=100$, and $M=5\times10^{18}$ are fixed. *G* is 4000, 5000, 6000, 7000, 8000, and 9000 (from right to left). (N) Dependence of *N*. $E=2900k$, $G=5000$, and $M=5\times10^{18}$ are fixed. *N* is 20, 40, 60, 80, 100, and 120 (from bottom to top). (M) Dependence of *M*. $E=2900k$, $G=5000$, and $N=100$ are fixed. *M* is 2, 4, 6, 8, 10×10^{18} (from bottom to top). Endothermic direction is upward.

Table 3
Best-fit parameters for each DSC endotherms

Sample	Annealing temperature (°C)	Best fit parameters					Calculated values	
		E (J)	N	G	M[a]	$N\times M$[a]	Peak (°C)	Half width (°C)
Wheat	20	3000k	42	8580	8.18×10^{18}	3.43×10^{20}	56.1	8.7
	50	3000k	125	7480	2.78×10^{18}	3.47×10^{20}	62.5	3.0
Corn	20	2900k	65	5100	7.32×10^{18}	4.76×10^{20}	65.2	6.1
	50	2900k	101	4980	4.82×10^{18}	4.87×10^{20}	66.6	3.9
Potato	20	2800k	71	4540	9.55×10^{18}	6.78×10^{20}	58.1	5.5
	50	2800k	107	4040	7.44×10^{18}	7.96×10^{20}	63.2	3.8

[a] g-Dry matter.

<0.1 °C for W_d, and 0 mW for H_p. The calculated curves fit the observed ones fairly well.

3.5. Effects of annealing temperature

The same value for E was found for both annealing temperatures, although E was on the order of $10k$ (J) in the calculations. This suggests that the energy making links was not influenced by annealing temperature. This fact is quite reasonable considering that hydrogen bonds are common bonding forces that form the double helices in amylopectin.

Starch samples annealed at 50 °C exhibited a greater value of N, smaller M, and a little smaller G than those annealed at 20 °C. The number of links in an ordered region (N) increased because annealing at a higher temperature produces more stable crystalline regions. It is likely that more links are required to stabilize the structure of crystalline regions. In contrast, the rotational freedom G decreased after treatment at a high temperature because many links formed in an ordered region inhibit the movement of chains. The number of ordered structures represented by M decreased with an increase in N. This is contrary to a statement by Tester et al. (1998) that annealing does not change the number of crystalline regions. A small value of M does not mean low total energy for gelatinization (i.e. the small ΔH) because it was offset by a large N.

Model calculation suggested that annealing at a higher temperature would produce more links in each ordered region of amylopectin and reduce the number of ordered regions; however the total numbers of links represented by the product ($N\times M$) does not change for corn and wheat and only slightly increases for potato. The different observations may be due to original crystalline polymorphs. Corn and wheat originally exhibit a more stable, closely packed A-polymorph, but potato has B-type crystals (Hizukuri, 1985). Annealing treatment at 50 °C may modify the B-type crystalline structure. According to Stute (1992), B-type crystals in potato starch were not changed by annealing, but A-type crystals were formed from B-types by heat-moisture treatment. The annealing may not produce an A-type structure from B-type potato starch, but more hydrogen bondings are formed by annealing at 50 °C.

3.6. Differences between A- and B-type starches

Comparing the three starches, the calculated E value was wheat > corn > potato. Only potato starch has a B-type polymorph, which is less stable than the A-type (Gidley & Bulpin, 1987; Knutson, 1990). The hydrogen bonding involved in the B-polymorph may require less energy for cleavage.

In contrast, the number of links in the system was wheat < corn < potato regardless of annealing temperatures. There are 3.7×10^{21} glucose units in 1 g starch. For both A- and B-type crystals, one interstrand hydrogen bond per glucose unit is formed (Imberty et al., 1988; Imberty & Pérez, 1988). In addition, there is one (A-type) or 0.5 (B-type) hydrogen bonding between two double helices in a crystalline region. This means that 1.5–2 hydrogen bondings per glucose unit may produce the ordered regions of amylopectin. The number of potential hydrogen bonds contained in 1 g dry starch was calculated as 5.3×10^{21} for wheat, 5.8×10^{21} for corn, and 4.3×10^{21} for potato starches according to amylopectin ratios in starch shown in Table 1 and reported crystal structure (Imberty et al., 1988; Imberty & Pérez, 1988). The ratio of actually formed links to the possible sites in amylopectin were given as the percentage of $M\times N$ values in Table 3 to the above calculated potential values. They were 6.5% for wheat, 8.6% for corn, and 16 or 18% for potato of glucose units in amylopectin that formed the ordered structure. The order (wheat < corn ≪ potato) was consistent with ratios of long chains (DP 13 and more) in amylopectin (Table 1), but the ratios of such long chains in amylopectin were much greater than the hydrogen bondings actually formed. In a model system of malto-oligomers, chains shorter than DP 10 did not crystallize (Gidley & Bulpin, 1987). A-type crystal was formed in DP 10–12, and the B-type pattern was found in DP 13- chains (Pfannemüller, 1987). Some parts of longer chains that easily crystallize are likely participants in the formation of A- or B-type crystalline regions.

4. Conclusion

We successfully explained the ordered structures of amylopectin using a uniform energy model. It is evident that annealing of starch produced different crystalline structures. Annealing at a high temperature is a physical process in the growth of an amylopectin crystalline structure by reorganizing its ordered structure to produce a smaller number of more highly ordered regions. It never changes the amylose-amylopectin ratio or chain length distribution. The number of hydrogen bonds in an A-type crystalline system was not influenced by annealing temperature, while additional hydrogen bonds may be formed in a B-type starch at a higher temperature. Energy distributions of hydrogen bondings in systems should be further considered even though the distributions are minimized by annealing.

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References

Atwell, W. A., Hood, L. F., Lineback, D. R., Varriano-Marston, E., & Zobel, H. F. (1988). The terminology and methodology associated with basic starch phenomena. *Cereal Food Worlds*, *33*, 306–311.

Biliaderis, C. G. (1990). Thermal analysis of food carbohydrates. In V. R. Harwalker, & C.-Y. Ma (Eds.), *Thermal analysis of foods* (pp. 168–220). London: Elsevier.

Biliaderis, C. G. (1991). The structure and interaction of starch with food constituents. *Canadian Journal of Physiology and Pharmacology*, *69*, 60–78.

Blanshard, J. M. V. (1987). Starch granule structure and function: A physicochemical approach. In T. Galliard (Ed.), *Starch: Properties and potential* (pp. 16–54). Chichester: Wiley.

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.

Gibson, T. S., Solah, V. A., & MacCleary, B. V. (1997). A procedure to measure amylose in cereal starches and flours with concanavalin A. *Journal of Cereal Science*, *25*, 111–119.

Gidley, M. J. (1987). Factors affecting the crystalline type (A–C) of native starches and model compounds: A rationalization of observed effects in terms of polymorphic structures. *Carbohydrate Research*, *161*, 301–304.

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

Gough, B. M., & Pybus, J. N. (1971). Effect on the gelatinization temperature of wheat starch granules of prolonged treatment with water at 50 °C. *Starch/Stärke*, *23*, 210–212.

Hizukuri, S. (1985). Relationship between the distribution of the chain length of amylopectin and the crystalline structure of starch granules. *Carbohydrate Research*, *141*, 295–306.

Hizukuri, S. (1986). Polymodal distribution of the chain lengths of amylopectins, and its significance. *Carbohydrate Research*, *147*, 342–347.

Hoover, R., & Vasanthan, T. (1994). The effect of annealing on the physicochemical properties of wheat, oat, potato and lentil starches. *Journal of Food Biochemistry*, *17*, 303–325.

Imberty, A., Chanzy, H., Pérez, S., Buléon, A., & Tran, V. (1988). A revisit to the three-dimensional structure of B-type starch. *Journal of Molecular Biology*, *201*, 365–378.

Imberty, A., & Pérez, S. (1988). The double-helical nature of the crystalline part of A-starch. *Biopolymers*, *27*, 1205–1221.

Jacobs, H., Eerlingen, R. C., Clauwaert, W., & Delcour, J. A. (1995). Influence of annealing on the pasting properties of starches from varying botanical sources. *Cereal Chemistry*, *72*, 480–487.

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.

Knutson, C. A. (1990). Annealing of maize starches at elevated temperatures. *Cereal Chemistry*, *67*, 376–384.

Kohyama, K., Matsuki, J., Yasui, T., & Sasaki, T. (2004). A differential thermal analysis of the gelatinization and retrogradation of wheat starches with different amylopectin chain lengths. *Carbohydrate Polymers*, *58*, 71–77.

Kohyama, K., & Nishinari, K. (1991). Effect of soluble sugars on the gelatinization and retrogradation of sweet potato starch. *Journal of Agricultural and Food Chemistry*, *39*, 1406–1410.

Koizumi, K., Fukuda, M., & Hizukuri, S. (1991). Estimation of the distribution of chain length of amylopectins by high-performance liquid chromatography with pulsed amperometric detection. *Journal of Chromatography*, *565*, 233–238.

Krueger, B. R., Knutson, C. A., Inglett, G. E., & Walker, C. E. (1987). A differential scanning calorimetry study on the effect of annealing on gelatinization behavior of corn starch. *Journal of Food Science*, *52*, 715–718.

Muhrbeck, P., & Svensson, E. (1996). Annealing properties of potato starches with different degrees of phosphorylation. *Carbohydrate Polymers*, *31*, 263–267.

Nagamine, T., & Komae, K. (1996). Improvement of a method for chain-length distribution analysis of wheat amylopectin. *Journal of Chromatgraphy A*, *732*, 255–259.

Nishinari, K., Koide, S., Williams, P. A., & Phillips, G. O. (1990). A zipper model approach to the thermoreversible gel–sol transition. *Journal of Physics, France*, *51*, 1759–1768.

Pfannemüller, B. (1987). Influence of chain length of short monodisperse amyloses on the formation of A- and B-type X-ray diffraction patterns. *International Journal of Biological Macromolecules*, *9*, 105–108.

Russell, P. L. (1987). Gelatinization of starches of different amylose/amylopectin content. A study by differential scanning calorimetry. *Journal of Cereal Science*, *6*, 133–145.

Stute, R. (1992). Hydrothermal modification of starches: The difference between annealing and heat/moisture-treatment. *Starch/Stärke*, *44*, 205–214.

Tester, R. F., & Debon, S. J. J. (2000). Annealing of starch—A review. *International Journal of Biological Mactromolecules*, *27*, 1–12.

Tester, R. F., Debon, S. J. J., & Karkalas, J. (1998). Annealing of wheat starch. *Journal of Cereal Science*, *28*, 259–272.

Tester, R. F., & Karkalas, J. (2001). The effects of environmental conditions on the structural features and physico-chemical properties of starches. *Starch/Stärke*, *53*, 513–519.