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Relationship between functionality and structure in barley starches

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Abstract

Normal and waxy barley grains were divided into eight fractions (A–H) from the surface layer to the center with a machine used to polish brewers' rice, respectively. The large, medium and small granule starches were isolated from the fractions. The functionalities of starches were examined in this study. The relationship between the functionalities of starch and the parameters of structure was also analyzed. The degree of hydrolysis increased in the order of large, medium and small granules in the same fraction both waxy and normal barley, but decreased from the surface to the center of grain with granule size. The small granule starches showed the greatest swelling power both waxy and normal barley in the three granule sizes, but was the easiest to gelatinize and to retrograde. The gel from large granules was the most stable both waxy and normal barley in the three granule sizes. Also the gel for waxy barley grain is more stable in the center than in the surface layer on the same class of granule size, whereas more stable for normal barley grain in the surface layer. The results of functionality gave good agreement with the structural parameter in the same origin of starches. The correlations among the functionality and parameter may be represented by a multiple regression equation ($r \geq 0.9$).

Keywords: Barley; Starch; Functionality; Structure; Correlation

1. Introduction

Starch is a major reserve polysaccharide of green plants and probably the second most abundant carbohydrate in nature next to cellulose. Much work has been done on structure and functionality of starches. Native starch granules present three levels of organization: macromolecular structure, crystal structure and ultrastructure. The macromolecular structure of many plant starches has been investigated in detail. These results were comprehensibly reviewed by Hizukuri (1996). In evaluating the functional properties of starch, the hydrolysis with enzyme, swelling power, gelatinization, pasting, retrogradation and gel properties are usually studied (Czuchajowska, Klamczynski, Paszczynska, & Baik, 1998; Jane et al., 1999; Kimura & Robyt, 1995; Klucinec & Thompson, 1999, 2002; Lauro, Forssell, Suortti, Hulleman, & Poutanen, 1999; Sasaki & Matsuki, 1998; Silverio, Fredriksson, Andersson, Eliasson, & Åman, 2000; Song & Jane, 2000; Tester & Karkalas, 1996; Tester & Morrison, 1990, 1992; Vasanthan & Bhatty, 1996; Wu & Seib, 1990; Yoshimoto, Takenouchi, & Takeda, 2002; Yoshimoto, Tashiro, Takenouchi, & Takeda, 2000; Zheng, Han, & Bhatty, 1998).

Recently, Tang, Ando, Watanabe, Takeda, and Mitsunaga (2000, 2001a,b) examined the physicochemical properties and structures of large, medium and small granule starches from waxy and normal barley fractions. The starches show great differences in water activity, gelatinization properties, relative crystallinity, amylose content and amylopectin structure with granule size and with fraction. Some linear correlations are also found between the parameters of structure and between the structure and properties of the starches. Tang, Watanabe, and Mitsunaga (2002a) also reported that the structures and properties of barley and quinoa starch are completely different although both are A type starches. Sasaki and Matsuki (1998) reported a linear correlation between swelling power and amylose content of 12 wheat starches, and a multiple correlation among swelling power, amylose content and amylopectin branch chain length (DP 6–12). Jane et al. (1999) investigated the gelatinization, pasting properties and amylopectin branch chain length of A, B, C-type starches (21 samples), but the relationship between the structure and property could not be expressed simply by a mathematical equation. It is considered that besides

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interference by lipids and other components with the properties of starch (Jane et al., 1999; Tester & Morrison, 1990, 1992), the way the structure of starch changes may differ from plant to plant, bringing about a specified interaction dependent on the molecular structure of the starches (Klucinec & Thompson, 1999). This may be the key to establishing the relation between the structure and functionality of starches of different plant origins.

In this study, we determined the functionality, hydrolysability with enzyme, gelatinization and retrogradation properties, swelling power and freeze–thaw stability of gels of starches from waxy and normal barley fractions. The functionalities were compared between varieties, among fractions, and among large, medium and small granule. The relationship was analyzed between the major parameters of structure and the functionality.

2. Experimental

2.1. Materials

The large, medium and small starch granules isolated from waxy barley (*Hordeum vulgare* L. emed. Yonezawa No. 2, six-rowed, grown in Okayama, Japan in 1996) and normal barley fractions (*H. vulgare* L. emed. Ichibanboshi, six-rowed, grown in Okayama, Japan in 1996) were used as described previously (Tang et al., 2000, 2001a). The fractions are indicated as A (100–90), B (90–80), C (80–70), D (70–60), E (60–50), F (50–40), G (40–30) and H (30–0) by a range of wt% of grain polished from the surface layer to the center. Starch granules were prepared by the modified alkali method as described previously (Tang et al., 2000, 2001b). The median sizes are 12.2–19.0 μm for large granules, 9.9 μm for medium granules and 2.0 μm for small granules in waxy barley, and large 18.4 μm, medium 12.3 μm and small 2.2 μm in normal barley, respectively. Defatted starch (nongranular starch) was prepared from the starch granules following the procedure of Takeda, Hizukuri, and Juliano (1986).

2.2. Susceptibility of starch granules to enzymes

Hydrolysis of starch granules with enzymes was done as reported previously (Tang et al., 2002a). To sample (25 mg) was added, successively, 1 ml of 0.1 M acetate buffer (pH 4.8), 100 units of beta-amylase (from barley, Sigma Chemical Co., St Louis, MO) and 700 units of isoamylase (from *Pseudomonas amyloderamosa*, Hayashibara Biochemical Laboratories, Inc., Okayama, Japan). The reaction was initiated at 37 °C with shaking for 0–30 h. It was stopped by the addition of 50 μl of 1 M HCl and then the pH returned to 7.0 with a 1 M NaOH solution, and then centrifuged at 7700*g* for 10 min. The supernatant was analyzed for soluble carbohydrate by the phenol-sulfuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). Percent hydrolysis was expressed as milligrams of maltose released per 100 mg of dry starch. Appropriate controls without the enzymes were prepared.

2.3. Swelling power of starches

Swelling power was evaluated by a modified version of the method of McCormuck, Panozzo, and Hong (1991). Starch granules (0.2 g) were weighed in glass tubes with coated screw caps to which 5 ml of a 0.1% $AgNO_3$ solution was added. The tubes were placed in a shaking water bath at 70 °C for 10 min and then transferred into a boiling water bath. After gelatinizing perfectly, the tubes were cooled in cold water (20 °C) for 5 min and centrifuged at 1700*g* for 4 min. The supernatant was removed carefully and swelling power was determined as sediment weight (g/g).

2.4. Stability of starch gel on freeze–thawing

The stability of starch gels was tested for freeze–thawing referring to the procedure of Wu and Seib (1990). Starch granules (0.2 g) were weighed in glass tubes with coated screw caps to which 5 ml of distilled water was added, and boiled for 1 h in a water bath with intense stirring for 1 min every 10 min. After cooling to room temperature (20 °C), the tubes containing starch pastes were stored at 4 °C for 24 h. After determination of free water from the samples, the tubes were put into a freezer at −20 °C for 22 h and thawed at 30 °C in a water bath for 2 h. After each cycle, triplicate tubes were centrifuged for 15 min at 1500*g*, and the amount of liquid separated was determined by weight.

2.5. Retrogradation of dispersed starch

The turbidity of nongranular starch was measured using the method of Klucinec and Thompson (1999). The 0.5% starch dispersion in 20% DMSO solution (v/v of water) was transferred into 1.5 ml glass cuvettes. The contents of the cuvettes were degassed at 20 °C (for 40 min) before the measurement of absorbance. The cuvettes containing dispersion were immersed in an ice water bath for 5 min, and absorbance was remeasured. The absorbance of the dispersion was measured every 5 min for 15 min while standing at 20 °C.

3. Results and discussion

3.1. Susceptibility of starch granules

The starch granules from waxy and normal barley were hydrolyzed for 30 h by conjugation of beta-amylase and isoamylase (Figs. 1 and 2). All the starch granules were initially hydrolyzed at a relatively fast rate from 0 to 5 h, followed by a slower rate up to 30 h. The degree of hydrolysis increased in the order of large, medium and small

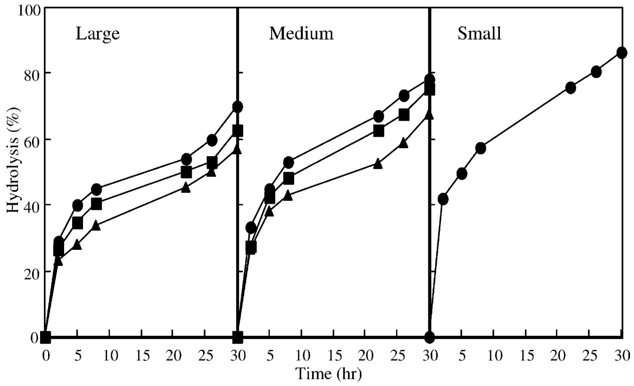

Fig. 1. Enzyme hydrolysis of waxy barley starch granules. (●) B fraction, (■) F fraction, (▲) H fraction.

granules in the same fraction in both waxy and normal barley. These results are similar to those for waxy and normal barley starches reported previously (Tang, Watanabe, & Mitsunaga, 2002b). Different rates in the early and the later parts of hydrolysis were also observed for acid and alpha-amylase hydrolysis (Vasanthan & Bhatty, 1996). This can be explained by considering that the enzymes attack the more amorphous regions of the starch granules initially, whereas the less accessible crystalline regions are hydrolyzed at a slower rate (Tang et al., 2002b). Also, both waxy and normal barley, the degree of hydrolysis decreased from the surface to the center of grain in the same class of granule size ($P < 0.05$). It is thought that these can be still interpreted from their structure (Table 1). We showed the faster hydrolysis rate (Hydrolysis-I, for 5 h) and slower hydrolysis rate (Hydrolysis-II, from 5 to 30 h) in Table 2 to quantitatively analyze the relation between the hydrolysis rate and structure of starch granules. Hydrolysis-I in normal starch was greater ($P < 0.01$) than that of waxy starch, but Hydrolysis-II was small ($P < 0.0005$). As for the normal starches having greater Hydrolysis-I, the high amylose content and low relative crystallinity are associated easily. However, the chain length distribution of amylopectin is most considered if want to interpret why small granule and waxy starch have a greater Hydrolysis-II, because the amylopectin with many short chains and few long chains may not be useful to form a stable cluster structure and crystalline network (Tang et al., 2002a).

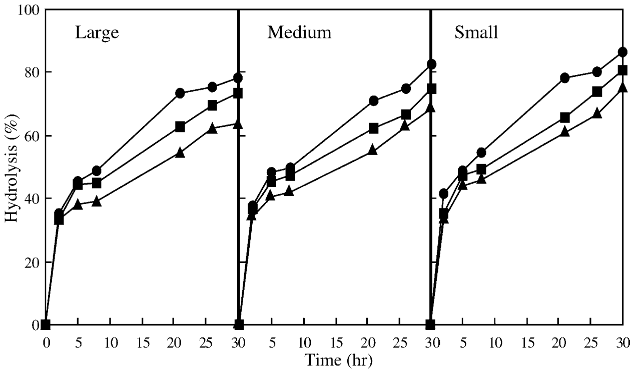

Fig. 2. Enzyme hydrolysis of normal barley starch granules. (●) C fraction, (■) F fraction, (▲) H fraction.

Table 1
Major structural characteristics of barley starches

Samples	Crystallinity (%)	Amylose (%)	DP_n[a]	SF[b]		SF/LF[c] (molar)
				Weight%	Molar%	
Waxy[d]						
B						
Large	28.6	8.5	8171	75.5	91.5	9.6
Medium	29.0	9.0	7043	78.4	91.0	10.5
Small	23.7	9.4	4657	79.1	90.6	12.3
F						
Large	34.7	4.0	11,481	76.1	96.0	9.9
Medium	33.9	3.7	8553	79.9	96.3	10.6
Small	32.5	2.2	6675	80.5	97.8	11.8
H						
Large	34.3	3.5	14,604	80.3	96.5	10.4
Medium	31.1	2.6	12,010	80.9	97.4	11.3
Small	30.8	1.4	6985	78.5	98.6	12.2
Normal[e]						
C						
Large	27.4	25.9	7883	67.7	90.7	9.8
Medium	22.6	24.6	7781	70.0	90.7	9.8
Small	23.3	21.9	7050	70.0	90.8	9.9
F						
Large	26.9	25.3	6881	71.0	90.6	9.6
Medium	22.5	25.7	6423	72.0	90.8	9.9
Small	24.7	22.0	6040	73.9	89.7	8.7
H						
Large	25.5	26.4	6078	72.2	89.3	8.3
Medium	21.4	25.4	6025	72.9	89.7	8.7
Small	25.0	22.4	5726	74.3	89.4	8.6

[a] Number-average degrees of polymerization of amylopectin.
[b] Short chain fraction of amylopectin.
[c] Molar ratio of short chain fraction (SF) to long chain fraction (LF) of amylopectin.
[d] Data from Tang et al. (2000, 2001a).
[e] Data from Tang et al. (2001b).

3.2. Swelling power of starches

The swelling power of barley fraction starches is given in Table 3. The swelling powers were 16.4–30.3 for waxy starch granules, and 13.3–18.9 for normal starch granules. The values of swelling power increased in the order of large, medium and small granule starches in the same fraction ($P < 0.1$) from both waxy and normal barley, but were greater in the waxy starch granules than normal starch granules ($P < 0.0005$). These observations were similar to those for waxy and normal barley starches reported previously (Tang et al., 2002b; Vasanthan & Bhatty, 1996). Also, the swelling power for waxy starches tended to increase from the surface to the center of grain, but to decrease for normal starches. Hydrogen bonds stabilizing the structure of the double helices in crystallites are broken

Table 2
Enzyme hydrolysis of barley starch granules

Samples	Hydrolysis-I[a]	Hydrolysis-II[b]
Waxy		
B		
Large	9.1	1.5
Medium	10.3	1.5
Small	11.8	1.6
F		
Large	8.0	1.4
Medium	9.4	1.5
Small	nd[c]	nd
H		
Large	6.6	1.4
Medium	8.6	1.4
Small	Nd	nd
Normal		
C		
Large	10.5	1.0
Medium	11.2	1.2
Small	11.6	1.4
F		
Large	10.2	1.0
Medium	10.6	1.2
Small	10.9	1.3
H		
Large	9.1	0.9
Medium	9.6	1.1
Small	10.2	1.2

Values are the mean of two separate measurements.

[a] Hydrolysis-I is the average hydrolysis weight proportion of starch granules per hour with enzymes for 5 h.

[b] Hydrolysis-II is the average hydrolysis weight proportion of starch granules per hour with enzymes from 5 to 30 h.

[c] Not determined.

Table 3
Gelatinization properties and swelling power of barley starches

Samples	Gelatinization[a]			Swelling power[b]
	T_p (°C)	ΔT (°C)	ΔH (J/g)	
Waxy				
B				
Large	63.3	13.4	7.6	16.4 ± 0.8
Medium	65.6	16.1	6.4	22.7 ± 0.9
Small	65.5	17.7	4.6	24.5 ± 1.6
F				
Large	65.2	9.9	12.6	22.5 ± 0.8
Medium	65.6	10.2	10.3	25.5 ± 1.0
Small	65.2	11.6	8.3	28.0 ± 1.4
H				
Large	64.8	9.6	10.8	25.8 ± 0.8
Medium	65.2	8.9	8.4	28.2 ± 1.5
Small	65.8	10.1	6.3	30.3 ± 1.6
Normal				
C				
Large	62.1	11.9	7.7	15.3 ± 0.4
Medium	62.2	15.2	5.7	16.3 ± 0.2
Small	64.5	15.7	5.0	18.9 ± 1.0
F				
Large	60.9	12.5	7.5	14.2 ± 0.1
Medium	61.2	14.2	5.5	16.3 ± 1.3
Small	63.6	15.3	5.3	18.6 ± 0.2
H				
Large	61.6	11.0	7.7	13.3 ± 1.2
Medium	62.6	16.9	5.8	
Small	64.0	17.5	5.4	

[a] Data from Tang et al. (2000, 2001b). T_p, peak temperature by DSC; ΔT, transition temperature range ($T_f - T_o$) by DSC; ΔH, enthalpy change by DSC.

[b] Values (g gel/g starch) are the mean ± SD of three separate measurements.

during gelatinization and replaced by hydrogen bonds with water (Tester & Karkalas, 1996). The swelling power of starch depends on the capacity of starch molecules to hold water via hydrogen bonding (Lee & Osman, 1991). But lipids and other components influence it simultaneously (Tester & Morrison, 1990). In this study, the samples were from the same plant, and separated by the same method. Accordingly, when hydrogen bonds in starch molecules after complete gelatinization are replaced by hydrogen bonds with water, the influence of lipids and other components may be the minor factors, and the amylose content and the proportion of outside-chains of amylopectin are the major factors stabilizing the gel structure to retain water (Tang et al., 2002b). These are qualitative interpretation and inference. It is not clear that each parameter of structure plays what role and shows how much action in the functionality. Accordingly, it is indispensable to establish a mathematical model between the functionality and structure in order to understand quantitatively.

3.3. Stability of starch gel on freeze–thawing

In freeze–thaw tests, little syneresis for the starch gels from H- and F-fractions of waxy barley was observed in the early freeze–thaw cycles, and then syneresis was induced suddenly (Fig. 3). The findings for H- and F-fraction starches were similar to those for waxy barley (WB and WB-X) starches reported previously (Wu & Seib, 1990). But the concentration of starch was lower in this study. Therefore, H- and F-fraction starch gels may have greater stability than WB and WB-X starch gels. However, the stability of B-fraction starch gel differed from that of H- and F-fraction starch gels. The syneresis of starch gel occurred rapidly in the early cycles, then slowed in B-fraction starch, probably due to its higher amylose content and smaller DP_n of amylopectin (Tang et al., 2000, 2001a). The starch gels from normal barley showed a faster syneresis in the early cycles and then a decrease (Fig. 4),

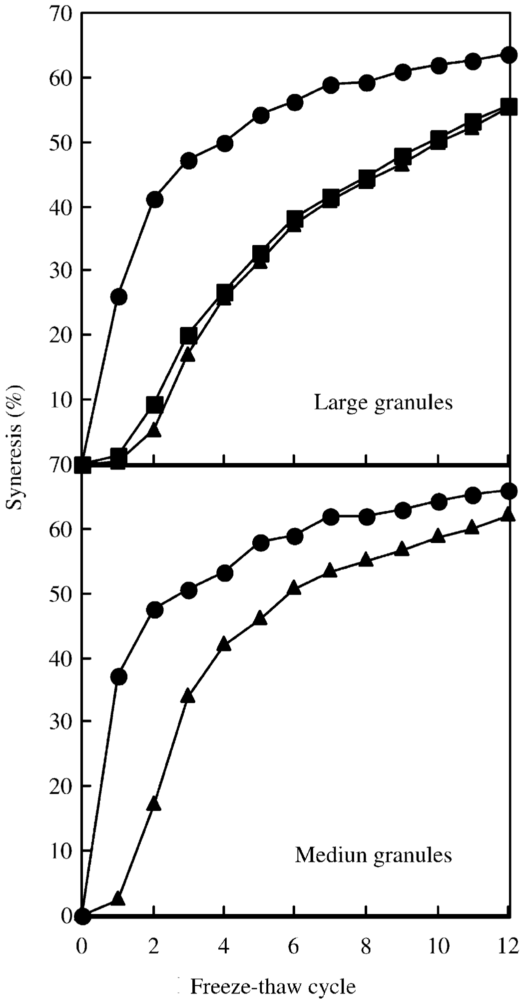

Fig. 3. Syneresis of waxy barley starch gels. (●) B fraction, (■) F fraction, (▲) H fraction.

similar to the B-fraction starches of waxy barley. The syneresis of starch gel had a greater difference among fractions for waxy barley, but a greater difference among granules for normal barley. To quantitatively analyze the relation between the stability of starch gel and structure of starch, the mean of syneresis of the first three cycles was calculated with Syneresis-I, and the mean of syneresis from the fourth to twelfth cycles with Syneresis-II (Table 4). Syneresis-I of waxy starch gels was smaller in large than medium granules in the same fraction, but Syneresis-II was greater. Syneresis-I of normal starch gels increased in the order of large, medium and small granules in the same fraction ($P < 0.1$), but Syneresis-II was smaller in small granules than in large and medium granules ($P < 0.05$). For the fractions of normal barley, Syneresis-I was smaller in the C-fraction than in H-fraction ($P < 0.1$). These results suggest that the gel from large granules is the most stable among the three granule sizes both in waxy and normal barley. Also the gel of waxy barley starch is more stable in the same class of granule size from the center of the grain than from the surface layer, whereas the gel of normal barley starch is more stable from the surface layer of grain. The findings can be explained by the amylose content of the starches, chain length distribution and molecular size of amylopectin (Table 1). When molecular sizes of amylopectin are too small, and the branch chains are too long like amylose or are too short, are disadvantageous in forming stable gel.

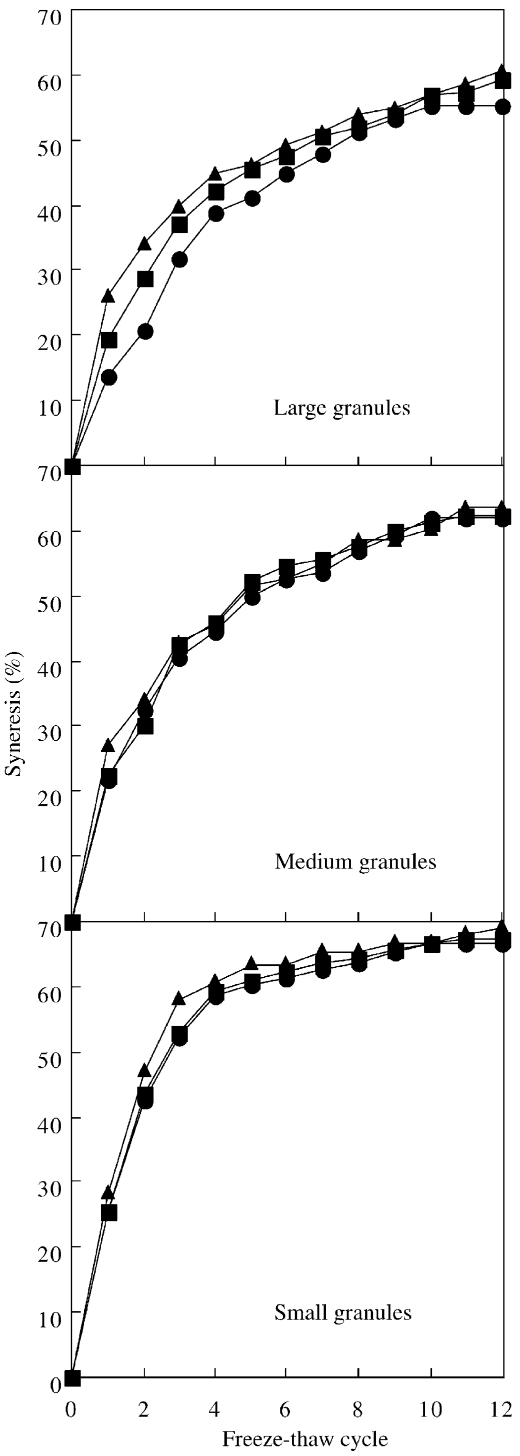

Fig. 4. Syneresis of normal barley starch gels. (●) C fraction, (■) F fraction, (▲) H fraction.

Table 4
Syneresis (wt%/time) of barley starch gels with freeze–thawing

Samples	Syneresis-I[a]	Syneresis-II[b]
Waxy		
B		
Large	15.7	1.8
Medium	16.9	1.7
Small	nd[c]	nd
F		
Large	6.7	4.0
Medium	nd	nd
Small	nd	nd
H		
Large	5.7	4.2
Medium	11.2	3.1
Small	nd	nd
Normal		
C		
Large	10.6	2.6
Medium	13.5	2.4
Small	17.4	1.6
F		
Large	12.4	2.5
Medium	14.2	2.2
Small	17.7	1.6
H		
Large	13.3	2.3
Medium	14.3	2.3
Small	19.4	1.2

Values are the mean of two separate measurements.

[a] Syneresis-I is average syneresis (wt%/time) of starch gels in the first three freeze–thaw cycles.

[b] Syneresis-II is average syneresis (wt%/time) of starch gels from the fourth to the twelfth freeze–thaw cycle.

[c] Not determined.

Table 5
Turbidity of 0.5% dispersions of nongranular starches in 20% DMSO–water (v/v)

Samples	Degassed at 20 °C for 40 min	Ice-water for 5 min	20 °C for 15 min
Waxy			
B			
Large	0.222 ± 0.068	0.341 ± 0.068	0.230 ± 0.068
Medium	0.397 ± 0.036	0.700 ± 0.036	0.390 ± 0.021
Small	0.617 ± 0.001	0.987 ± 0.008	0.642 ± 0.034
F			
Large	0.187 ± 0.043	0.283 ± 0.057	0.201 ± 0.033
Medium	0.216 ± 0.043	0.326 ± 0.048	0.237 ± 0.068
Small	0.448 ± 0.040	0.599 ± 0.080	0.454 ± 0.035
H			
Large	0.143 ± 0.058	0.161 ± 0.037	0.143 ± 0.060
Medium	0.161 ± 0.064	0.236 ± 0.087	0.163 ± 0.059
Small	0.346 ± 0.015	0.527 ± 0.079	0.361 ± 0.027
Normal			
C			
Large	0.123 ± 0.040	0.567 ± 0.032	0.169 ± 0.036
Medium	0.184 ± 0.025	0.755 ± 0.011	0.203 ± 0.056
Small	0.223 ± 0.022	0.884 ± 0.005	0.316 ± 0.060
F			
Large	0.115 ± 0.033	0.537 ± 0.073	0.130 ± 0.035
Medium	0.119 ± 0.006	0.714 ± 0.035	0.127 ± 0.002
Small	0.310 ± 0.062	0.977 ± 0.094	0.323 ± 0.063
H			
Large	0.138 ± 0.022	0.861 ± 0.038	0.175 ± 0.019
Medium	0.187 ± 0.056	1.092 ± 0.110	0.205 ± 0.059
Small	0.298 ± 0.069	1.107 ± 0.095	0.326 ± 0.044

Values are the mean ± SD of four separate measurements.

3.4. Retrogradation of dispersed starch

Because complete dispersion of amylose and high-amylose starches in water requires heating to temperatures in excess of 150 °C, the turbidity development of starch is examined in a binary solvent of DMSO and water generally (Klucinec & Thompson, 1999). In our study, to observe the retrogradation behavior of barley starches, the turbidity of barley starch dispersions in DMSO–water solvent was determined at different temperatures (Table 5). The turbidity of the waxy starch dispersions was similar after degassing and rewarming for 15 min at room temperature. The values increased in the order of large, medium and small granules in the same fraction ($P < 0.05$), and decreased from the surface layer to the center of grain ($P < 0.01$). The turbidity of the starch dispersions increased slightly after cooling in the ice-water bath, compared to that after degassing and rewarming for 15 min. The turbidity of the normal starch dispersions was 0.123–0.310 after degassing, and 0.169–0.326 after rewarming for 15 min, and the value of the latter significantly larger ($P < 0.01$). But both increased in the order of large, medium and small granules in the same fraction ($P < 0.05$). The turbidity of the starch dispersions increased greatly after cooling in the ice-water bath, compared to that after degassing and rewarming. Also, the values in the center were higher than those of the surface layer ($P < 0.05$). The waxy starches had higher values than the normal starches in the steps of degassing and rewarming for 15 min ($P < 0.05$), but lower in the steps of the ice-water bath ($P < 0.01$), probably due to a lower amylose content (Tang et al., 2002b). The results suggest that the small granule starches were the easiest to retrograde both in normal and waxy barley. The observations agreed with previous reports (Klucinec & Thompson, 1999; Tang et al., 2002b). However, judging from general consideration, the retrograde property of the small granule starches seems to contradict their swelling powers. This is interpreted as having a higher molar concentration in the starch dispersions and gels of small granules (Tang et al., 2002b). In order to explain it well, it is thought that the parameter of structure of starches, amylose content, molecular weight distribution, chain distribution of

Table 6
Linear regression equations between functionality and structure of barley starches

n	Equation[a]	Coefficient[b]
16	$Y_1 = 16.3550 - 0.2395X_1$	−0.7658
16	$Y_1 = 8.5715 + 0.0786X_2$	0.5595
16	$Y_1 = 13.2296 - 0.00043X_3$	−0.8240
16	$Y_1 = 40.9866 - 0.3387X_5$	−0.6959
16	$Y_2 = 0.7993 + 0.0180X_1$	0.3730
16	$Y_2 = 1.5670 - 0.0171X_2$	−0.7866
16	$Y_2 = -1.3852 + 0.0358X_4$	0.6971
16	$Y_2 = -0.0597 + 0.1367X_6$	0.6664
18	$Y_3 = 57.5601 + 0.2266X_1$	0.5923
18	$Y_3 = 65.8573 - 0.1384X_2$	−0.8510
18	$Y_3 = 39.7335 + 0.3205X_4$	0.8028
18	$Y_3 = 54.5386 + 0.9192X_6$	0.6524
18	$Y_4 = 27.8318 - 0.5288X_1$	−0.7892
18	$Y_4 = 11.0260 + 0.1487X_2$	0.5218
18	$Y_4 = 19.5110 - 0.0008X_3$	−0.6927
18	$Y_4 = 75.3058 - 0.6704X_5$	−0.7619
18	$Y_5 = -4.6469 + 0.4309X_1$	0.8611
18	$Y_5 = 8.9718 - 0.1159X_2$	−0.5448
18	$Y_5 = 2.0092 + 0.0007X_3$	0.7741
18	$Y_5 = -30.7422 + 0.4104X_5$	0.6244
18	$Y_6 = 27.5 - 0.4729X_2$	−0.9025
18	$Y_6 = 14.0572 + 0.0008X_3$	0.3888
18	$Y_6 = -63.5216 + 1.1185X_4$	0.8698
18	$Y_6 = -17.5613 + 3.7730X_6$	0.8336
18	$Y_7 = 0.3683 + 0.0190X_2$	0.6564
18	$Y_7 = 1.4120 - 0.0001X_3$	−0.8250
18	$Y_7 = 6.7425 - 0.0658X_5$	−0.7344
18	$Y_7 = 1.6096 - 0.0952X_6$	−0.3800
14	$Y_8 = 10.1530 + 0.1896X_2$	0.4576
14	$Y_8 = 23.2549 - 0.0012X_3$	−0.8124
14	$Y_8 = 112.0303 - 1.0742X_5$	−0.7403
14	$Y_8 = 33.3460 - 2.0581X_6$	−0.4283
14	$Y_9 = 3.2662 - 0.0495X_2$	−0.5444
14	$Y_9 = 0.1155 + 0.0003X_3$	0.8647
14	$Y_9 = -21.3820 + 0.2592X_5$	0.8145
14	$Y_9 = -2.2966 + 0.4863X_6$	0.4614

[a] Y_1 : hydrolysis-I, Y_2 : hydrolysis-II, $Y_3 = T_p$, $Y_4 = \Delta T$, $Y_5 = \Delta H$, Y_6 : swelling power, Y_7 : turbidity of dispersion starch in ice-water, Y_8 : syneresis-I, Y_9 : syneresis-II. X_1 : relative crystallinity (%) of starch granules, X_2 : amylose content (%) of starch, X_3 : number-average degrees of polymerization (DP_n) of amylopectin, X_4 : weight proportion (%) of short chain fraction (SF) in amylopectin, X_5 : molar proportion (%) of short chain fraction (SF) in amylopectin, X_6 : molar ratio of short chain fraction to long chain fraction (LF) in amylopectin.

[b] $P < 0.05$ for all values.

amylopectin and interaction among components must be considered generally.

3.5. Correlation between functionality and structure

Starch is primarily composed of two glucose polymers, amylose and amylopectin. Different crystals are formed depending on the percentages and structure of components. The functionalities of starch are a synthetic representation of these parameters. We have investigated the percentage and structure of the components in barley fraction starches (Tang et al., 2000, 2001a,b). The major structures, relative crystallinity, amylose content, DP_n and chain length distribution of amylopectin change in the law for the starches, although it differ with genotype, with fraction and with granule size (Table 1). The gelatinization properties of the starches have good correlations with their structures (Tang et al., 2001a,b). In this study, the linear correlations among the functionalities and parameters of waxy and normal starches were analyzed. The four major regression equations of each functionality are given in Table 6. The statistical analysis suggests that these linear correlations among the functionalities and parameters are appropriate, although the coefficients were lower ($r < 0.5$) between Hydrolysis-II (Y_2) and relative crystallinity (X_1), swelling power (Y_6) and DP_n of amylopectin (X_3), turbidity (Y_7) and molar of SF/LF (X_6), Syneresis-I (Y_8) and amylose content (X_2) or X_6, Syneresis-II (Y_9) and X_6. The difference of these coefficients seemed to reflect the difference in the role and action that each parameter plays in the functionalities of starch within the experimental error. The correlations corresponded with the said qualitative interpretation and inference. Accordingly, the correlations among the functionalities and parameters may be represented by a multiple regression equation (Table 7). The coefficient reached at

Table 7
Multiple regression equations between functionality and structure of barley starches

n	Equation[a]	Coefficient[b]
16	$Y_1 = -0.6765 - 0.1596X_1 - 0.0059X_2 - 0.0004X_3 + 0.1984X_5$	0.8642
16	$Y_2 = 5.1132 - 0.0451X_1 - 0.0433X_2 - 0.0236X_4 - 0.0136X_6$	0.9257
18	$Y_3 = 71.9885 - 0.1561X_1 - 0.2024X_2 + 0.0062X_4 - 0.1327X_6$	0.8763
18	$Y_4 = 95.3108 - 0.4663X_1 - 0.2324X_2 - 0.0002X_3 - 0.6954X_4$	0.9116
18	$Y_5 = -4.3913 + 0.5500X_1 + 0.0896X_2 + 0.0003X_3 - 0.0741X_4$	0.9354
18	$Y_6 = -33.1702 - 0.1206X_2 + 0.0002X_3 + 0.4695X_4 + 1.8846X_6$	0.9484
18	$Y_7 = 3.4918 + 0.0019X_2 - 0.0001X_3 - 0.0231X_5 - 0.0149X_6$	0.8782
14	$Y_8 = 74.0147 - 0.2628X_2 - 0.0016X_3 - 0.5535X_5 + 0.8151X_6$	0.8926
14	$Y_9 = -17.1968 + 0.0494X_2 + 0.0003X_3 + 0.2065X_5 - 0.2563X_6$	0.9264

[a] Y_1 : hydrolysis-I, Y_2 : hydrolysis-II, $Y_3 = T_p$, $Y_4 = \Delta T$, $Y_5 = \Delta H$, Y_6 : swelling power, Y_7 : turbidity of dispersion starch in ice-water, Y_8 : syneresis-I, Y_9 : syneresis-II. X_1 : relative crystallinity (%) of starch granules, X_2 : amylose content (%) of starch, X_3 : number-average degrees of polymerization (DP_n) of amylopectin, X_4 : weight proportion (%) of short chain fraction (SF) in amylopectin, X_5 : molar proportion (%) of short chain fraction (SF) in amylopectin, X_6 : molar ratio of short chain fraction to long chain fraction (LF) in amylopectin.

[b] $P < 0.05$ for all values.

least 0.9 in all equations ($P < 0.05$). These findings are useful for the quantitative understanding of the complicated properties of starch. If the interaction among parameters and other minor parameters too are considered, a more complete equation may be provided.

4. Conclusions

The present results indicated that the functionalities of barley starches differed with granule size and with location in the grain. The functionalities were well consistent with the parameters of starch structure. Their correlations may be represented by a multiple regression equation. The findings suggest that it is possible to construct a mathematical model of the relation between the functionality and structure of starches of the same plant origin, although it is difficult to find a universal law for all starches. Such these mathematical models provide concrete and effective grounds for the genetic engineering of starch and breed improvement of cereals.

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