Food Chemistry 74 (2001) 407–415

Food Chemistry

www.elsevier.com/locate/foodchem

Rapid communication

Starch from hull-less barley: II. Thermal, rheological and acid hydrolysis characteristics

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Received 14 November 2000; received in revised form 16 May 2001; accepted 16 May 2001

Abstract

Gelatinization, granular swelling, amylose leaching, viscosity and acid susceptibility characteristics of starches isolated from 10 hull-less barley (HB) genotypes [zero amylose (CDC Alamo), waxy (CDC candle, SB 94794, SB 94912, and SB 94917), normal amylose (Phoenix, CDC Dawn, SR 93102, and SB 94860) and high amylose (SB 94893 and SB 94897)] were monitored by differential scanning calorimetry (DSC), swelling power (SP), solubility, Brabender viscoamylography, and reaction with 2.2 N HCl (at 35 °C), respectively. DSC data showed that T_o, T_p, T_c, T_c–T_o, and ΔH ranged from 50.1–56.1, 58.1–64.5, 71.0–75.8, 17.9–24.0 °C and 9.6–14.2 J/g of amylopectin, respectively. In compound waxy (SB 94917) and compound normal (SR 93102 and SB 94860) starches, T_o and T_c–T_o were lower and higher, respectively, than in the other starches. ΔH followed the order: compound normal > waxy > normal≈zero amylose > high amylose > compound waxy. The SP followed the order: zero amylose > waxy > compound normal > normal > high amylose. A rapid increase in solubility occurred at lower temperatures (< 70 °C) for zero amylose HB starch, however, this increase was gradual for the other starches. At 90 °C, solubility followed the order: high amylose > compound normal > normal > waxy. Zero amylose and waxy HB starches exhibited lower pasting temperatures, higher peak viscosities, and higher viscosity breakdown than normal HB starches. The extent of acid hydrolysis followed the order: zero amylose > compound waxy > waxy > normal > compound normal > high amylose. High correlations were observed between physicochemical properties and structural characteristics of HB starches. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hull-less barley; Starch; Physicochemeical property

1. Introduction

Researches on barley starches (Czuchajowska, Klamczynski, Paszczynska, & Baik, 1998; Kang, Sugimoto, Kato, Sakamoto, & Fuwa, 1985; Lorenz & Collins, 1995; Morrison, Scott, & Karkalas, 1986; Morrison, Tester, Snape, Law, & Gidley, 1993; Song & Jane, 2000; Tester & Morrison, 1992; Vasanthan & Bhatty, 1996; Yoshimoto, Tashiro, Takenouchi, & Takeda, 2000) have revealed that starches from different genotypes vary widely in structure, composition and properties. However, similar studies have not been carried out on hull-less barley (HB) starches. In a previous study, we evaluated the granule morphology, chemical composition, granule size distribution and amylopectin structure of starches from 10 HB genotypes grown at Saskatoon, Saskatchewan, Canada (Li, Vasanthan, Rossnagel, & Hoover, 2001). These starches differed with respect to amylose content, bound lipid content, proportion of small granules, granule morphology, and amylopectin structure. Compound granules were found in certain genotypes, which were clusters of a few granules but looked like single granules. This study was undertaken to characterize structure–property relationships for these same HB genotypes. At present, in North America, maize starch is intensively used in a number of food and industrial applications. Therefore, this study was also intended to compare barley starches with waxy and normal maize starches.

2. Materials and methods

2.1. Materials

Barley samples from four registered cultivars (CDC Alamo, CDC candle, CDC Dawn, and Phoenix) and six

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0308-8146/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0308-8146(01)00247-3

breeding lines (SB 94912, SB 94917, SR 93102, SB 94860, SB 94893, and SB 94897) of HB grown and harvested at Saskatoon in 1998 were obtained from the Crop Development Center, University of Saskatchewan, Saskatoon, Canada. Commercial waxy and normal maize starches were purchased from A.E. Staley Manufacturing Company (Decatur, IL).

2.2. Starch isolation

Starch was isolated from barley grains according to the method of Wu, Sexson, and Sanderson (1979).

2.3. Gelatinization characteristics

Starch gelatinization was studied on a Mettler (TA 4000) differential scanning calorimeter. Water (15 μl) was added with a micro syringe to starch (5 mg, db) in aluminium differential scanning calorimetry (DSC) pans, which were then hermetically sealed and allowed to stand overnight at room temperature. The scanning temperature range and the heating rate were 30–110 °C and 10 °C/min, respectively. The thermograms were recorded with water as reference. Indium was used for calibration.

2.4. Brabender viscoamylography

Pasting characteristics (6% w/v, pH 6.5) of the starches were determined using a viscoamylograph (C.W. Brabender Instruments, Inc., South Hackensack, NJ) equipped with a 700 cm/g cartridge, operating at a bowl speed of 75 rpm. The starch slurry was heated from 30 to 96 °C at the rate of 1.5 °C/min, maintained at 96 °C for 30 min, and then cooled to 51 °C at the same rate.

2.5. Swelling power and solubility

Swelling power and solubility were carried out in the range of 60–90 °C according to the method of Li and Corke (1999).

2.6. Acid hydrolysis

The starches were hydrolyzed with 2.2 N HCl at 35 °C (1.0 g starch/40 ml acid) for 18 days in a shaking water bath at 35 °C. Details of the procedure has been described elsewhere (Vasanthan & Bhatty, 1996).

2.7. Statistical analysis

Data reported are means of at least duplicate determinations. Data were analyzed using the SAS System for Windows version 8 (SAS Institute Inc., Cary, NC). Significance levels were used at $P<0.1$, $P<0.05$, and $P<0.01$.

3. Results and discussion

3.1. Gelatinization characteristics

The gelatinization transition temperatures [onset (T_o), mid-point (T_p), and conclusion (T_c)] and gelatinization enthalpy (ΔH) are presented in Table 1. T_o, T_p, T_c, T_c-T_o, and ΔH were in the ranges of 50.1–56.1, 58.1–64.5, 71.0–75.8, 17.9–24.0 °C, and 9.6–14.2 J/g of amylopectin, respectively, in HB starches. Compound HB starches (SB 94917, SB 94860, and SR 93102) exhibited a lower T_o (50.1–51.2 °C) and a wider T_c-T_o (21.9–24.0°C) than other HB starches. Compound waxy HB starch (SB 94917) exhibited the lowest ΔH (9.6 J/g of amylopectin), whereas, the highest ΔH (13.5–14.2 J/g of amylopectin) was recorded for compound normal starches (SR 93102 and SB 94860) (Table 1). T_o, T_p, T_c, T_c-T_o and ΔH were 59.8, 66.9, 77.8, 18.0 °C, and 15.5 J/g of amylopectin, respectively, for normal maize starch. The corresponding values for waxy maize starch were 60.6, 67.1, 78.1, 17.6 °C, and 13.3 J/g of amylopectin. Correlation analysis (Table 2) with previous data (Li et al., 2001) showed that T_o was positively correlated with starch granule size ($r=0.63$, $P<0.05$), short branch chains (DP5–17; $r=0.67$, $P<0.05$) and negatively correlated with small granule (diameter $\leqslant 10$ μm) size ($r=-0.64$, $P<0.05$), the proportion of small granules by number ($r=-0.70$, $P<0.05$) and by weight ($r=-0.70$, $P<0.05$), long branch chains (DP$\geqslant$35) ($r=-0.78$, $P<0.01$) and average branch chain length ($r=-0.75$, $P<0.05$). T_c–T_o was positively correlated with small granule size ($r=0.86$, $P<0.01$), the proportion of small granules by number ($r=0.57$, $P<0.1$) and by weight ($r=0.86$, $P<0.01$), long branch chains ($r=0.78$, $P<0.01$) and average branch chain length ($r=0.84$, $P<0.01$) and negatively correlated with short branch chains (DP5–17; $r=-0.91$, $P<0.01$). ΔH was negatively correlated with portion of small granules by weight ($r=-0.65$, $P<0.05$) and T_p ($r=-0.62$, $P<0.05$). The influence of granular size on ΔH was also reported by Tang, Ando, Watanake, Takeda, and Mitrunga (2000) for waxy barley starch. They showed that ΔH decreases with decreasing granule size. Significant correlations between average branch chain length and T_o has also been reported for other starches (Jane, Chen, McPherson, Wong, Radosavlijevic, & Kasemsuwan, 1999; Shi & Seib, 1992; Wang, White, & Pollak, 1993; Yuan, Thompson, & Boyer, 1993). Cooke and Gidley (1992) suggested that ΔH primarily reflects the loss of double helical order rather than loss of X-ray crystallinity, while Tester and Morrison (1990) postulated that the DSC endotherm gives a measure of crystallite quality (effectively double helix length) from T_p and overall crystallinity (quality×quantity) from ΔH. Biliaderis, Maurice, and Vose (1980) suggested that T_c–T_o is influenced by the degree of branching of amylopectin (the greater the degree of branching, the wider the melting temperature range). It is likely, that T_c–T_o could also indicate the degree of heterogeneity of the starch crystallites. This study indicated that T_c–T_o (Table 1) was influenced to a large extent by the proportion of small granules (Li et al., 2001). For instance, starches containing a high proportion of small granules (compound and high amylose HB starches) exhibited the widest T_c–T_o (Table 1). Small granules have been shown to contain more amylose (Czuchajowska, Szczodrak, & Pomeranz, 1992; Li et al., 2001), longer (DP$\geqslant$35) amylopectin branches (Li et al., 2001), and lower ΔH (Tang et al., 2000) than larger granules. This suggests that the DSC endotherm of small granule starches could be influenced by the interplay of: (1) disordering of double helices of short chains from amylopectin; (2) disordering of double helical chains formed by interaction between amylose and amylopectin chains (average chain length > 17.9; Li et al., 2001); and (3) disordering of V-helix residues of amylose–lipid complexes [the bound lipid content in SB 94917, SR 93102, SB 94860, SB 94893, and SB 94897 are higher than in other starches used in this study (Li et al., 2001)]. It is likely, that differences in size, form and order of double helices and single V-helix residues of amylose–lipid complexes may be the factors responsible for the broad melting endotherm of small granule starches.

Jenkins (1994) has shown, by small angle X-ray scattering studies on normal maize, waxy maize and high-amylose maize starches, that amylose acts to disrupt the packing of the amylopectin double helices within the crystalline lamellae. A reduction in crystalline lamella was observed with increase in amylose content. He postulated that the disrupting effect of amylose on amylopectin could be due to co-crystallization between amylose and amylopectin or to penetration of amylose into the amorphous regions of the cluster (where the branch points are located). This suggests that the energy (ΔH) required for unravelling and melting of the double helices within the crystalline lamella may decrease with increasing amylose content. Recently, Hoover and Manuel (1996) have shown that the ΔH of maize starches (waxy maize > normal maize > high amylose maize) is influenced by their amylose content. In this study, ΔH followed the order: compound normal > waxy > normal > high amylose≈zero amylose > compound waxy, indicating that other factors, such as proportion of small granules, may also reflect the differences in ΔH.

3.2. Swelling power and solubility

The swelling power (SP) and solubility of the starches are presented in Figs. 1 and 2, respectively. Compound waxy (SB 94917) and waxy (CDC Candle and SB 94912) HB exhibited a two-stage swelling pattern, whereas a single-stage swelling pattern was shown by the other starches (Fig. 1). SP increased with raising temperature from 60 to 90 °C. The increase in SP was very rapid for zero amylose (CDC Alamo) HB and waxy maize starch, and occurred at relatively low temperatures (60–70 °C; Fig. 1). SP, in the other starches at higher temperature (> 70 °C), followed the order: compound waxy HB (SB 94917) > waxy HB (CDC Candle)≈waxy HB (SB 94912) > normal maize > compound normal HB (SR 93102)≈normal HB (Phoenix)≈normal HB (CDC Dawn) > high amylose HB (SB 94897)≈high amylose HB (SB 94893). The increase in SP (within the temperature range 60–70 °C) was rapid for compound waxy HB (SB 94917), waxy HB (CDC Candle), and waxy HB (SB 94912) starches, but was gradual for normal HB, high-amylose HB and normal maize starches (Fig. 1). A rapid increase in solubility occurred at lower temperatures (< 70 °C) for zero amylose (CDC Alamo) and waxy maize starches (Fig. 2). However, the increase

Table 1
Thermal characteristics[a] of hull-less barley and maize starches

Line analyzed	Starch type	T_o (°C)	T_p (°C)	T_c (°C)	T_c–T_o (°C)	ΔH (J/g)
CDC Alamo	Zero-amylose waxy	54.5	61.8	74.5	20.0	12.6
CDC Candle	Waxy	55.4	61.9	73.8	18.4	13.1
SB 94912	Waxy	56.1	62.1	75.8	19.7	13.1
SB 94917	Compound waxy	50.5	64.5	74.5	24.0	9.6
SR 93102	Compound normal	50.1	59.9	72.0	21.9	13.5
SB 94860	Compound normal	51.2	60.9	73.5	22.4	14.2
Phoenix	Normal	53.1	59.1	71.0	17.9	12.8
CDC Dawn	Normal	52.0	58.1	72.5	20.5	12.7
SB 94893	High-amylose	53.0	62.3	74.3	21.3	11.8
SB 94897	High-amylose	53.3	61.7	74.4	21.2	12.2
Waxy maize	Waxy	60.6	67.1	78.1	17.6	13.3
Normal maize	Normal	59.8	66.9	77.8	18.0	15.5
LSD[b]		0.8	0.9	1.1	1.6	1.7

[a] T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; T_c–T_o, gelatinization temperature range; ΔH, gelatinisation enthalpy in J/g of amylopectin.

[b] Least significant difference at $P < 0.05$.

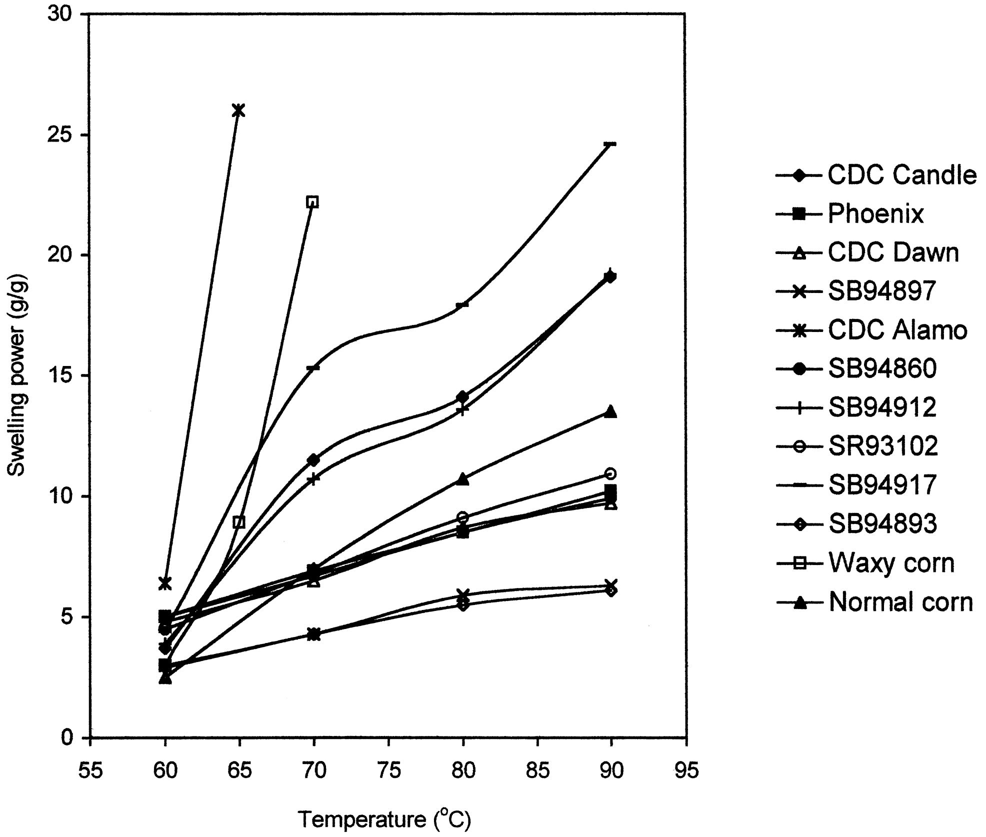

Fig. 1. Swelling power of native hull-less barley and maize starches.

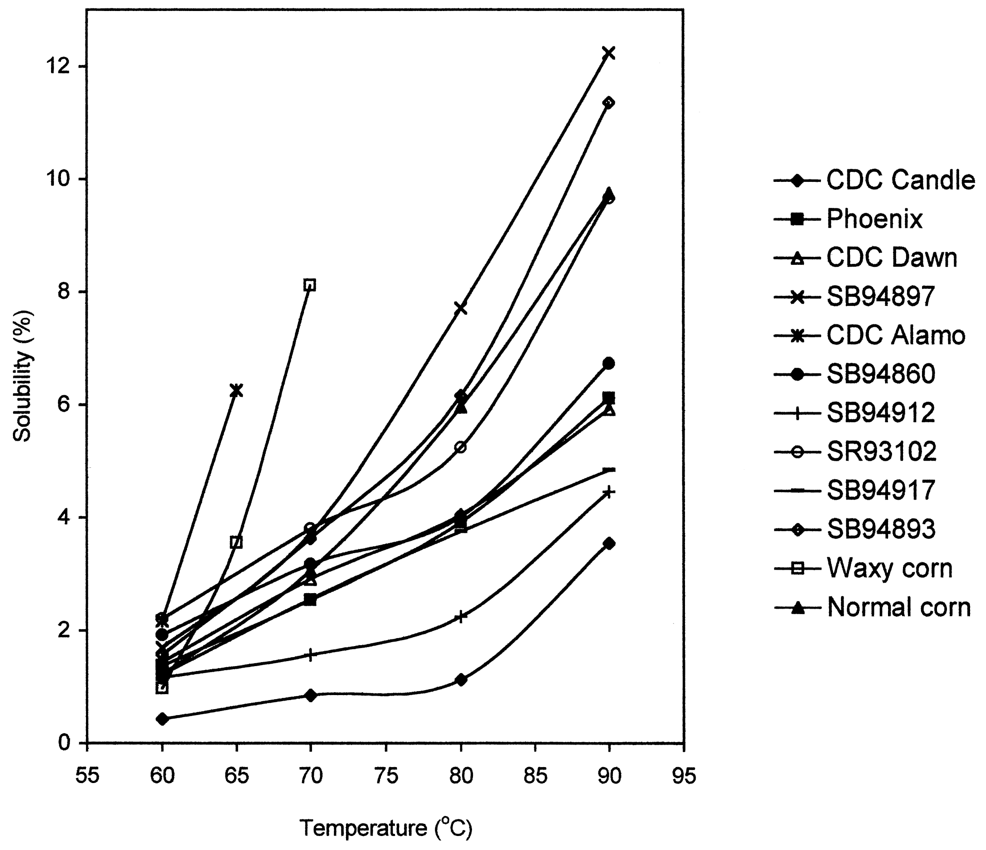

Fig. 2. Solubility curves of native hull-less barley and maize starches.

in solubility was gradual for the other starches. At 90 °C, the solubility followed the order: high amylose HB (SB 94897) > high amylose HB (SB 94893) > normal maize > compound normal HB (SR 93102) > compound normal HB (SB 94860) > normal HB (Phoenix) > normal HB (CDC Dawn) > compound waxy HB (SB 94917) > waxy HB (SB 94912) > waxy HB (CDC Candle). Linear regression analysis (Table 2) showed that SP was negatively correlated with amylose content ($r=-0.94$ at 90 °C, $P<0.01$) and total lipids ($r=-0.81$, $P<0.01$). Solubility (at 90 °C) was positively correlated with amylose content ($r=0.91$, $P<0.01$), total lipids ($r=0.76$, $P<0.05$), and negatively correlated with swelling power ($r=-0.78$, $P<0.05$).

The difference in SP and solubility between the starches can be attributed to the interplay of the following factors: (1) the level of lipid-complexed amylose chains (Tester & Morrison, 1992) [high amylose HB (CDC Alamo) > compound normal HB (SB 94860) > high amylose HB (SB 94893) > compound normal HB (SR 93102) > normal maize > normal HB (Phoenix) > waxy HB (SB 94912) > normal HB (CDC Dawn) > waxy maize > compound waxy (SB 94917) > waxy HB (CDC Candle; Li et al., 2001)]; (2) molar proportion of amylopectin unit chains of DP 6-24 (Shi & Seib, 1992) [DP5–17 and DP18–34 ranged from 48.2–59.1 and 31.4–38.0%, respectively, in the starches used in this study (Li et al., 2001)]; (3) total amylose content (Sasaki & Matsuki, 1998) [SB 94893 > SB 94897 > SB 94860 > SR 93102 > Phoenix > normal maize > CDC Dawn > SB 94912 > SB 94917 > CDC Candle > waxy maize > CDC Alamo (Li et al., 2001)]; and (4) extent of interaction between starch chains within the amorphous and crystalline domains (Hoover & Manuel, 1996).

Several researchers have shown that cereal starch granules do not show complete swelling until amylose has been leached from the granule (Bowler, Williams, & Angold, 1980; Doublier, 1981). Hermannson and Svegmark (1996) have shown, by microscopy, that the swelling pattern of potato amylopectin starch differs from that of normal potato starch. They showed that potato amylopectin starch does not exhibit structures typical of swollen gelatinized granules (at 60 °C); instead it transforms immediately into a macromolecular solution. This indicates that amylose restrains swelling and maintains the integrity of swollen granules. Furthermore, lipid-complexed amylose chains have been shown to restrict both granular swelling and amylose leaching (Tester &

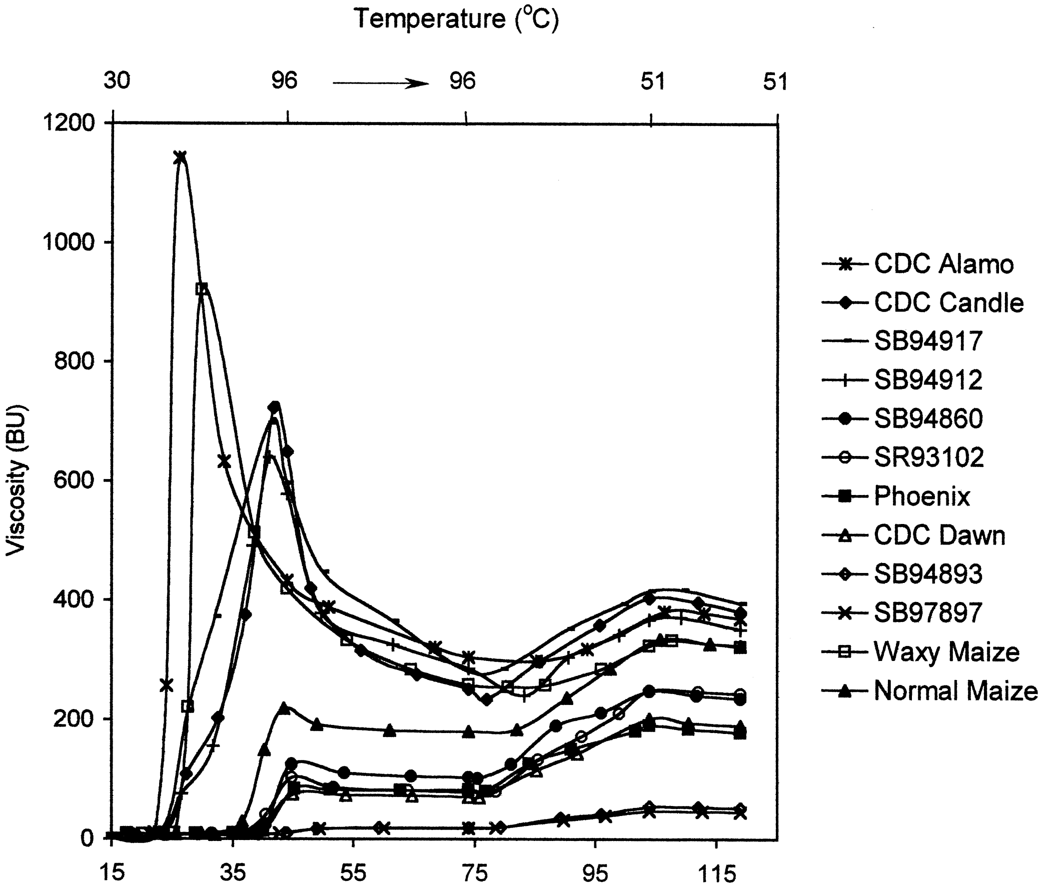

Fig. 3. Pasting properties of native hull-less barley and maize starches.

Table 2
Correlations (r value[a]) between physicochemical properties[b] and structural characteristics[c] of hull-less barley starches

	Amylose	Lipids	BL	SGS	GS	SGN	SGW	T_o	T_p	T_c	T_c–T_o	ΔH	SP	S	AH	DP5–17	DP18–34	DP$\geqslant$35
Lipids	0.90***																	
BL	0.92**	1.00***																
SGS	0.31	0.42	0.42															
GS	−0.65**	−0.38	−0.43	−0.28														
SGN	0.59*	0.37	0.42	0.49	−0.96***													
SGW	0.30	0.24	0.26	0.74**	−0.69**	0.81***												
T_o	−0.36	−0.28	−0.28	−0.64**	0.63**	−0.70**	−0.70**											
T_p	−0.32	−0.16	−0.17	0.38	0.12	0.04	0.51	0.14										
T_c	−0.31	−0.19	−0.18	0.18	0.34	−0.25	0.12	0.48	0.76**									
T_c–T_o	0.17	0.17	0.18	0.86***	−0.44	0.57*	0.86***	−0.73**	0.44	0.25								
ΔH	0.14	0.28	0.25	−0.10	0.47	−0.49	−0.65**	0.20	−0.62**	−0.29	−0.44							
SP	−0.94***	−0.81***	−0.83***	−0.01	0.37	−0.22	0.12	0.16	0.57	0.39	0.11	−0.41						
S	0.91***	0.76**	0.80***	0.34	−0.61*	0.57	0.43	−0.29	−0.05	−0.04	0.29	−0.01	−0.78**					
AH	−0.98***	−0.88***	−0.90***	−0.28	0.66**	−0.59*	−0.30	0.36	0.35	0.36	−0.13	−0.20	0.94***	−0.93***				
DP5–17	−0.11	−0.09	−0.10	−0.85***	0.37	−0.55	−0.81***	0.67**	−0.47	−0.21	−0.91***	0.36	−0.21	−0.16	0.09			
DP18–34	−0.31	−0.16	−0.18	0.20	0.45	−0.43	0.12	0.15	0.58*	0.64**	0.33	−0.11	0.21	0.11	0.33	−0.32		
DP$\geqslant$35	0.24	0.17	0.19	0.79***	−0.60***	0.77***	0.78***	−0.78***	0.19	−0.11	0.78***	−0.32	0.17	0.10	−0.23	−0.87***	−0.19*	
CL	0.17	0.10	0.11	0.81***	−0.53	0.71**	0.78***	−0.75**	0.28	0.01	0.84***	−0.37	0.21	0.08	−0.14	−0.92***	−0.06	0.99***
PT	0.98***	0.84***	0.86***	0.22	−0.66**	0.56*	0.23	−0.41	−0.46	−0.40	0.15	0.17	−0.96***	0.84***	−0.95***	−0.67	−0.33	0.20
PV	−0.96***	−0.79**	−0.83**	−0.21	0.65*	−0.59	−0.10	0.56	0.72**	0.74**	−0.06	−0.38	0.95***	−0.75*	0.95***	0.08	0.73**	−0.46
TP	0.67*	0.64*	0.71*	0.22	−0.64*	0.61	0.25	−0.39	−0.34	−0.45	0.09	0.16	−0.96***	0.72*	−0.74**	−0.18	−0.67*	0.52
BD	−0.95***	−0.78**	−0.82**	−0.24	0.68*	−0.63*	−0.16	0.58	0.67*	0.72**	−0.10	−0.33	0.93***	−0.76**	0.94***	0.13	0.73**	−0.51
SB	0.20	0.44	0.48	0.34	−0.23	0.26	0.33	−0.18	0.12	0.04	0.23	0.16	0.30	0.09	−0.39	−0.27	−0.10	0.33

[a] *,**, and *** = significant at $P < 0.1$, 0.05, and 0.01, respectively.

[b] BL, bond lipids extracted by hot 1-propanol–water; SGS, small granule size (average small granule diameter); GS, granule size (average granule diameter); SGN, proportion of small granules (granule diameter $\leqslant 10$ μm) by number; SGW, proportion of small granules by weight; T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; T_c–T_o, transition temperature range; ΔH, enthalpy; SP, swelling power at 90 °C; S, solubility at 90 °C; AH, extent of acid hydrolysis after 12 days; PT, pasting temperature; PV, peak viscosity; TP, pasting peak temperature; BD, breakdown; SB, setback; DP5–17, DP18–34, and DP$\geqslant$35, degree of polymerization 5–17, 18–34, and $\geqslant$35, respectively; CL, average chain length of debranched amylopectin.

[c] See Li et al. (2001) in this issue.

Morrison, 1992). Thus, differences in SP (Fig. 1) and solubility (Fig. 2) between (1) zero amylose (CDC Alamo) and waxy maize starches, (2) zero amylose and the other waxy HB starches (SB 94917, SB 94912, and CDC Candle), (3) the waxy HB starches, and (4) waxy and normal HB starches can be explained. It is unlikely, that the molar proportion of amylopectin chains DP5–17 could be a major factor influencing SP and solubility, since this parameter does not differ significantly among the starches (Li et al., 2001).

3.3. Pasting properties

The Brabender viscoamylograms of HB and maize starches are presented in Fig. 3. Zero amylose (CDC Alamo) and waxy HB starches (CDC Candle, SB 94912, and SB 94917) exhibited lower pasting temperatures (63.0–64.5 °C), higher peak viscosities (640–1142 BU), and higher viscosity breakdown (424–843 BU; during the holding cycle at 95 °C) than normal HB starches. The corresponding values for normal (SR 93102, SB 94860, Phoenix, and CDC Dawn) HB starches were 82.5–88.1 °C, 75–125 BU and 4–24 BU, respectively. Similar differences were also found between waxy and normal maize starches (Fig. 3). Pasting temperature was correlated with amylose content ($r=0.98$, $P<0.01$), total lipid ($r=0.84$, $P<0.01$), SP ($r=-0.96$, $P<0.01$), and solubility ($r=0.84$, $P<0.01$). Peak temperature was correlated with amylose ($r=0.67$, $P<0.1$), total lipid ($r=0.64$, $P<0.1$) and amylopectin chains of DP18–34 ($r=-0.67$, $P<0.1$; Table 2). The peak viscosity was negatively correlated with amylose ($r=-0.96$, $P<0.01$), total lipid ($r=-0.79$, $P<0.05$), SP ($r=0.95$, $P<0.01$), solubility ($r=-0.75$, $P<0.1$) and amylopectin chains of DP 18–34 ($r=-0.73$, $P<0.05$; Table 2). Viscosity breakdown during the holding cycle at 96 °C was negatively correlated with amylose ($r=-0.95$, $P<0.01$), total lipid ($r=-0.78$, $P<0.05$) and solubility ($r=-0.76$, $P<0.05$) and positively correlated with amylopectin chain length of DP 18–34 ($r=0.73$, $P<0.05$) and SP ($r=0.93$, $P<0.01$). Waxy HB and waxy maize starches showed higher peak viscosity than normal and high amylose starches (Fig. 3). This can be attributed to trace quantities of amylose and bound lipids in waxy genotypes (Li et al., 2001). This seems plausible, since the highest viscosity was shown by zero amylose HB starch.

The difference in the extent of breakdown in viscosity between the waxy and non-waxy HB starches (Fig. 3) can be explained on the basis of differences in SP [waxy HB > non waxy HB (Fig. 2)] and extent of amylose leaching [non waxy HB > waxy HB (Fig. 3)]. The granules of waxy HB starches would be highly susceptible to disintegration during the holding period (at 96 °C), due to direct contact between highly swollen granules. However, granules of non-waxy HB starches would be more resistant to disintegration due to lower granular swelling (Fig. 2) and less friction between swollen granules (the granules would be surrounded by a network of leached amylose chains, which would hinder granule-granule contact).

3.4. Acid hydrolysis

The solubilization patterns of the starches are presented in Fig. 4. A relatively high rate was observed during the first 10 days, followed by a slower rate thereafter. At the end of the 10th day of hydrolysis (corresponding mainly to the degradation of the amorphous region of the granule), zero amylose (CDC Alamo), compound waxy HB (SB 94917), waxy HB (CDC Candle), normal HB (Phoenix), compound normal HB (SB 94860), normal HB (CDC Dawn), high amylose HB (SB 94893), and high amylose HB (SB 94897) were hydrolyzed to the extents of 40.2, 39.3, 37.8, 34.8, 34.9, 34.7, 31.5, and 30.9%, respectively. The corresponding values for normal maize and waxy maize were 32.6 and 36.8%, respectively. Differences in the extent of hydrolysis between the starches were more pronounced beyond the 10th day (corresponding to the degradation of the crystalline region). The extent of hydrolysis at the end of the 18th day of hydrolysis followed the order: CDC Alamo (47.6%) > SB 94917 (46.6%) > SB 94912 (46.2%) > CDC Candle (45.1%) > CDC Dawn (43.7%)≈Phoenix (43.6%) > SB 94860 (43.0%) > SR93102 (42.0%) > SB 94893 (39.6%)≈SB 94897 (39.7%). Among the maize starches, waxy maize was hydrolyzed (45.1%) to a greater extent than normal maize (42.0%).

Correlation analysis (Table 2) indicated that the extent of acid hydrolysis negatively correlated with total lipids ($r=-0.88$, $P<0.01$), amylose content ($r=-0.98$, $P<0.01$), solubility ($r=-0.93$, $P<0.01$) and positively correlated with granule size ($r=0.66$, $P<0.05$), ΔH ($r=0.82$, $P<0.01$), and SP ($r=0.94$, $P<0.01$). No correlation was found with amylopectin branch chain length (Table 2).

Differences in the extent and rate of hydrolysis between starches during the initial stages (1–10 days) of hydrolysis have mainly been attributed to differences in: (1) granule size [small granules are hydrolyzed faster and to a greater extent than larger granules (Vasanthan & Bhatty, 1996)]; (2) amount of lipid-complexed amylose chains [lipid-complexed amylose chains resist degradation by H_3O^+ (Morrison, Tester, Gidley, & Karkalas, 1993)]; (3) double helical content [Morrison et al., 1993 showed by ^{13}C/CP/MAS–NMR that double helix content increases (due to retrograded free amylose) on lintnerization of non-waxy barley starches but was little changed for waxy barley starches]; and (4) extent of interaction between starch chains (Hoover & Manuel, 1996) within the amorphous domains of the granule

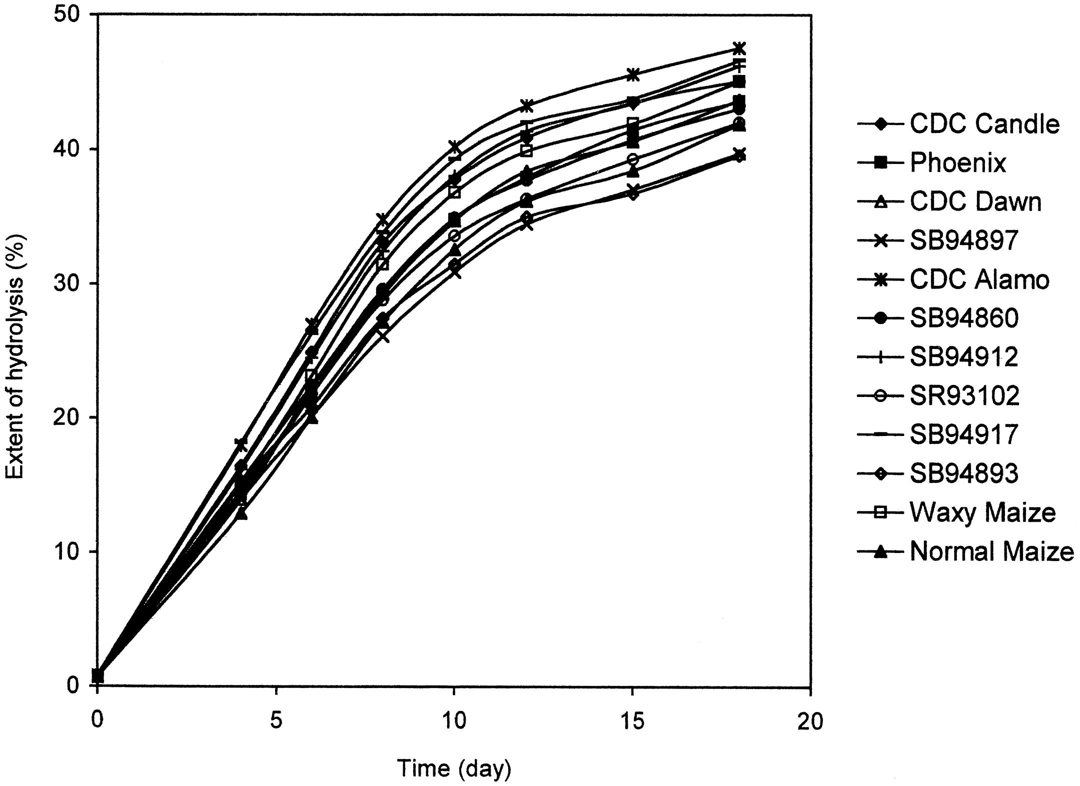

Fig. 4. Acid hydrolysis (2.2 N HCl at 35 °C) of native hull-less barley and maize starches.

[presence of double helices and close packing of non-helical amylose chains within the amorphous regions will hinder the conformational transformation (chair→half chair) required for protonation of glycosidic oxygens (Hoover, 2000; Hoover & Manuel, 1996)].

In this study, the observed differences cannot be explained solely on the basis of small granule content (SB 94917 > SB 94897 > SR 93102 > SB 94893 > Phoenix > CDC Dawn > SB 94860 > SB 94912 > CDC Candle > CDC Alamo > waxy maize≈normal maize), level of amylose—lipid complexes (SB 94897 > SB 94860 > SB 94893 > SR 93102 > normal maize > Phoenix > SB 94912 > CDC Dawn > CDC Candle > waxy maize≈SB 94917 > CDC Alamo, double helical content or amylose–amylose interactions. We postulate that the observed differences in hydrolysis between the starches during the first 10 days of hydrolysis are probably influenced by the interplay of the above factors.

The hydrolysis pattern beyond the 10th day (Fig. 4), suggests that the starches differ with respect to the organization of the double helical chains within their crystalline domains. To account for the slower hydrolysis rate of the crystalline domains of the starch granule, two hypotheses have been proposed (French, 1984; Kainuma & French, 1971). First, the dense packing of starch chains within the starch crystallites does not readily allow the penetration of H_3O^+. Second, acid hydrolysis of a glucoside bond requires a change in conformation (chair→half chair) of the D-glycopyranosyl unit. Obviously, if the crystalline structure immobilizes the sugar conformation, then this transition (chair→half chair) would be difficult. This transition would become even more difficult if crystallites are formed by association between linear amylose chains. (AMY–AMY) and/or between amylose and the outer branches of amylopectin (AMY–AMP). The lower extent of hydrolysis observed for the high amylose (SB 94893 and SB 94897) HB starches (Fig. 4) reflect crystallites formed by association between AM–AM and AMY–AMP chains.

4. Conclusion

This study has shown that the physicochemical properties of HB starches are influenced to different extent by the interplay of: (1) small granule size; (2) proportion of small granules by number and weight; (3) level of amylose—lipid complexes; (4) amylose content; (5) magnitude of interaction between starch chains within the amorphous and crystalline domains; and (6) double helical content. Work is in progress to determine the influence of physical modification such as heat–moisture treatment and annealing on the structure and properties of HB starches.

Acknowledgements

The authors gratefully acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC), Canadian Wheat Board and the Saskatchewan Agriculture Development Fund. We also acknowledge the expert technical assistance of Mr. D. Hassard from University of Saskatchewan.

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